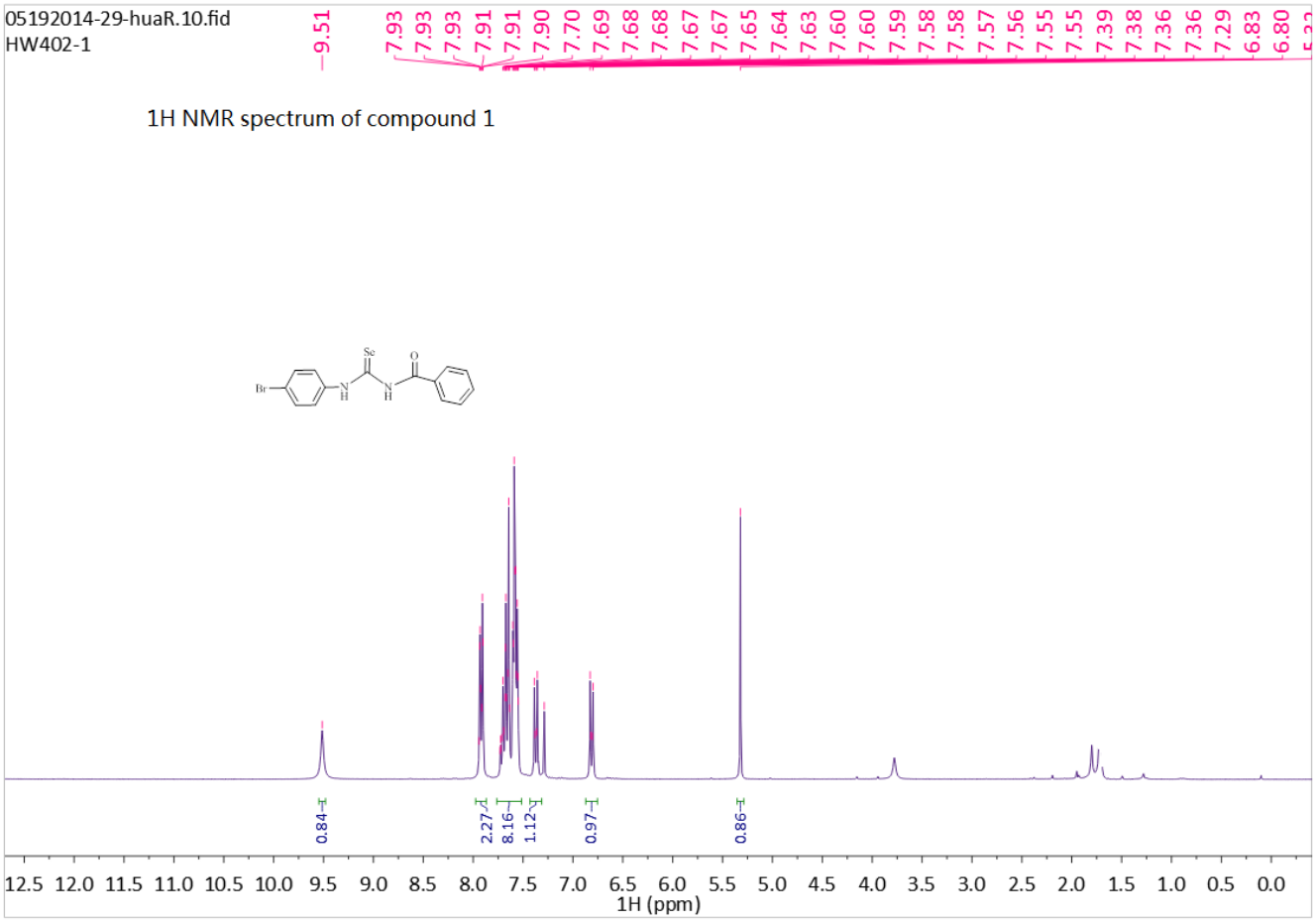
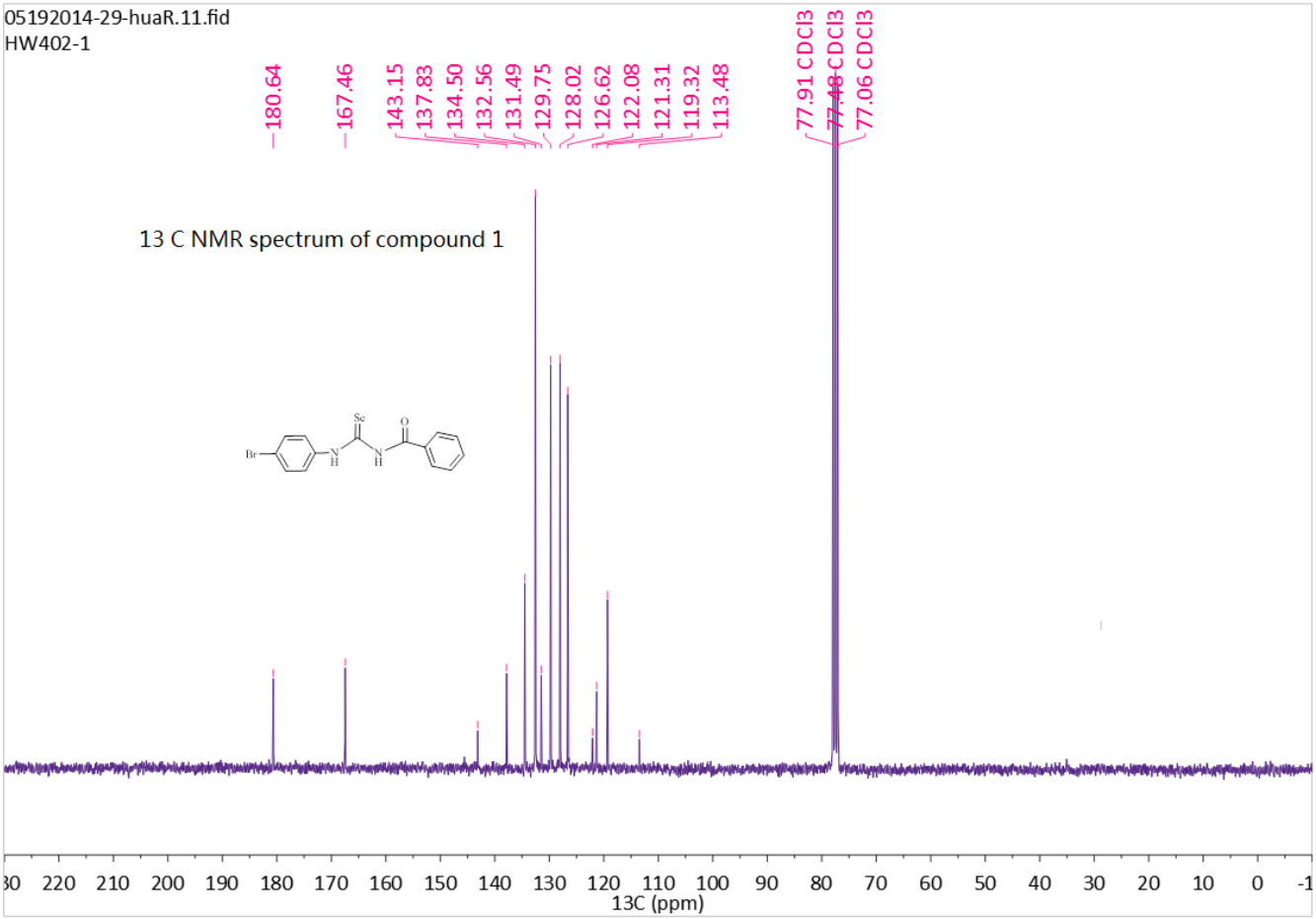
Supporting Information

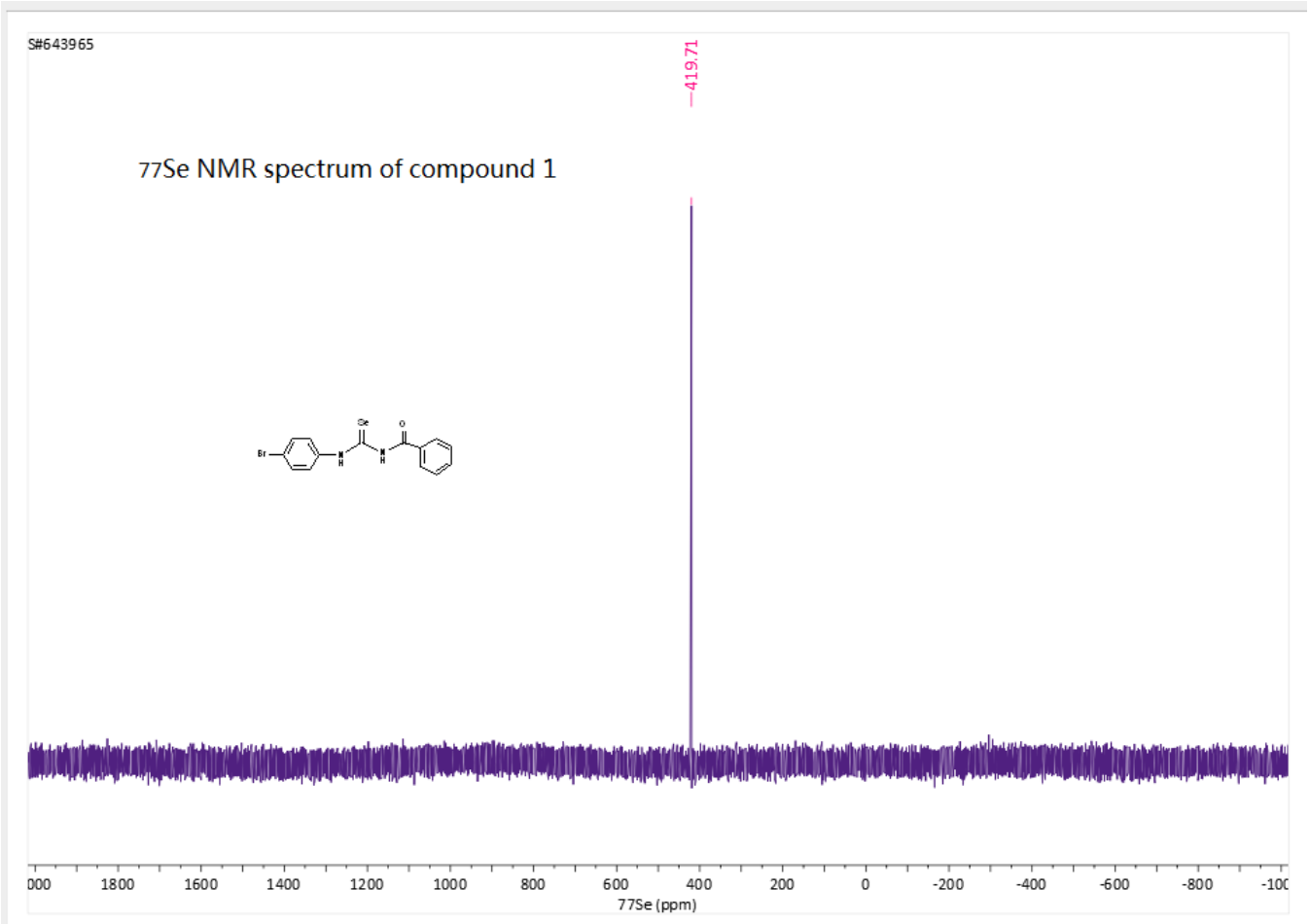
New Insight into the Chemistry of Selenoureas: Synthesis and Single Crystal Structural Study of Diverse Derivatives

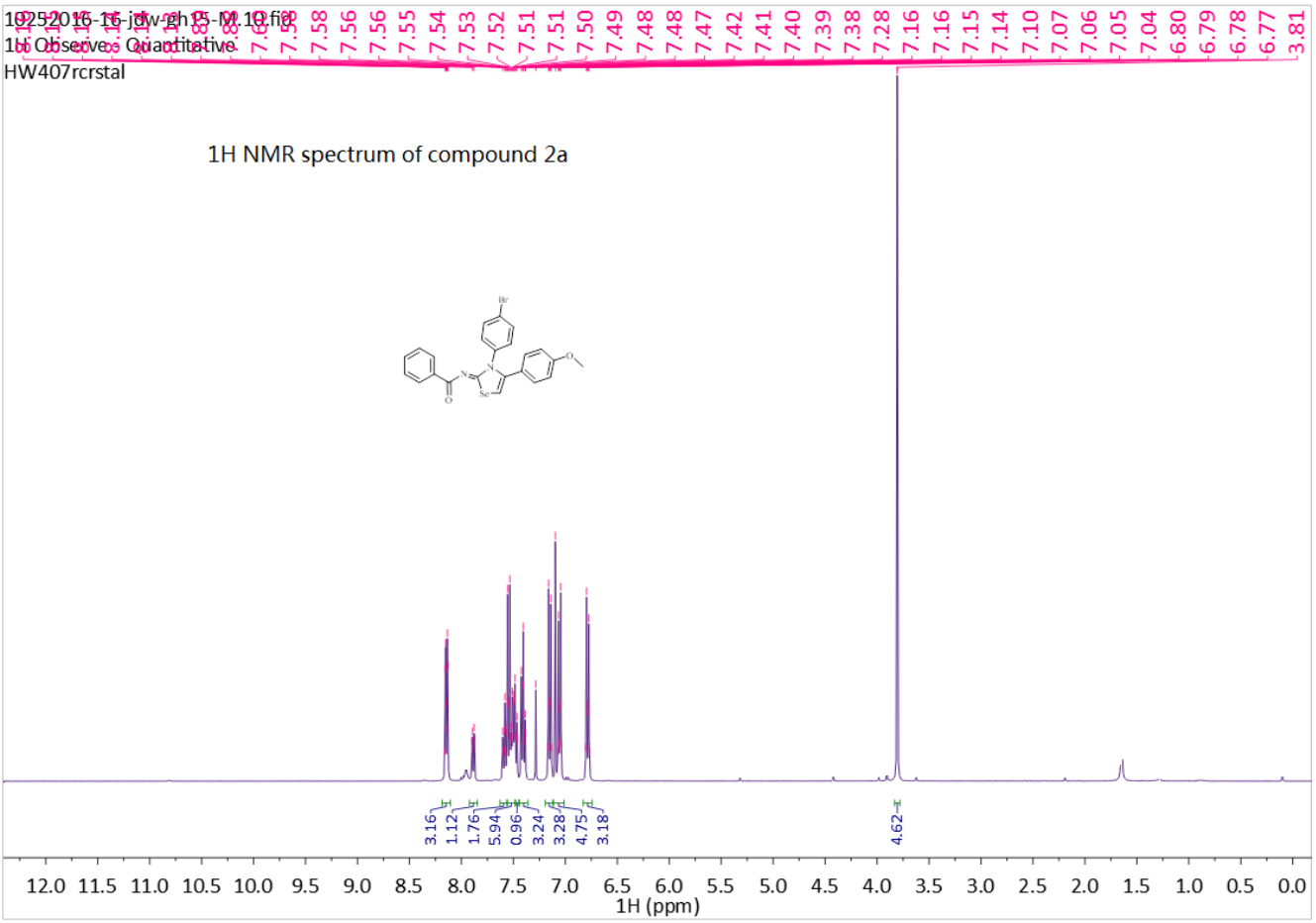
*Guoxiong Hua, Junyi Du, Cameron L. Carpenter-Warren, David B. Cordes, Alexandra M. Z. Slawin and J. Derek Woollins**

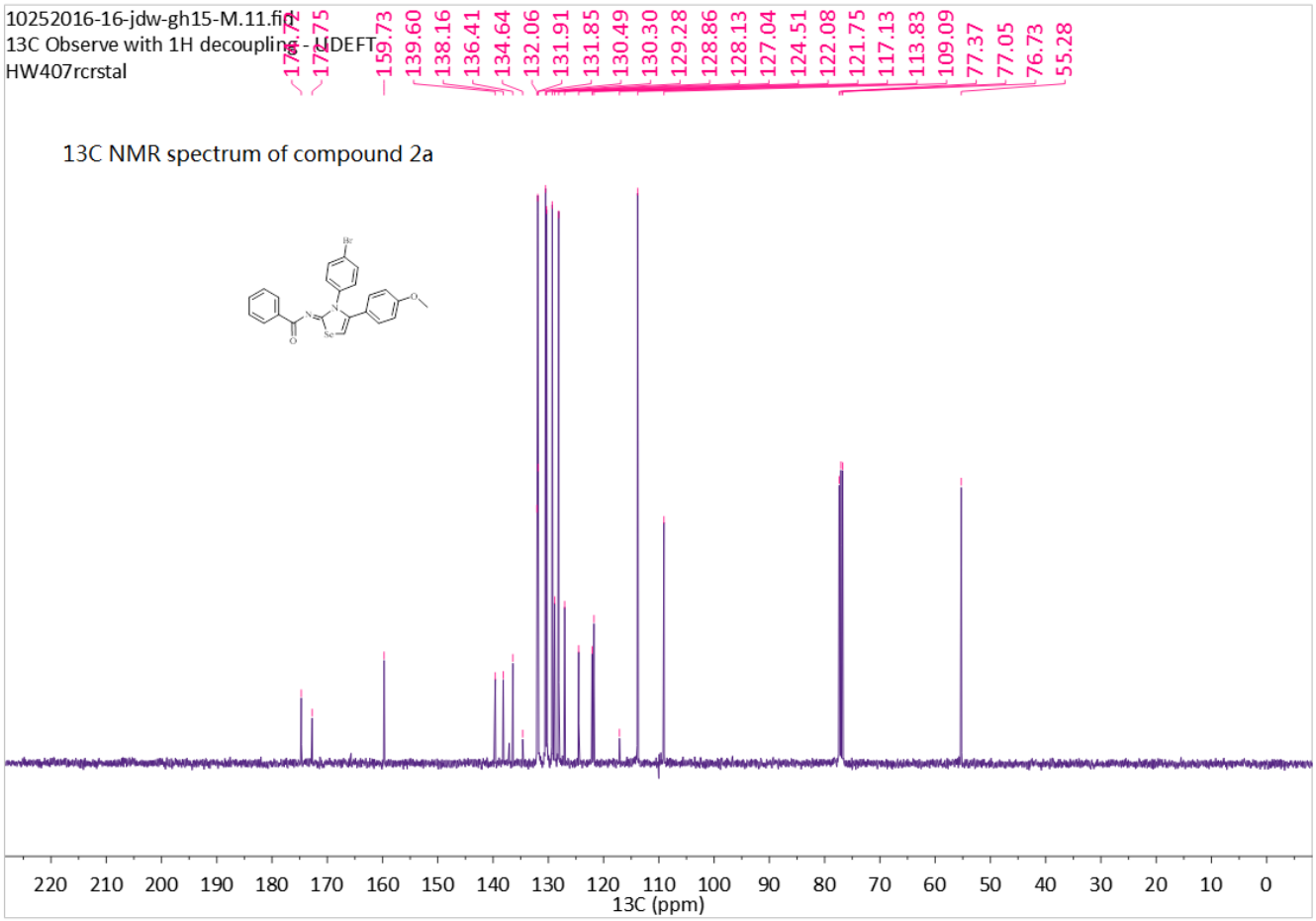
1. ^{1}H, ^{13}C and ^{77}Se NMR spectra of compounds 1, 2a-c, 3, 4, 6, 8, 9 and 10a-d

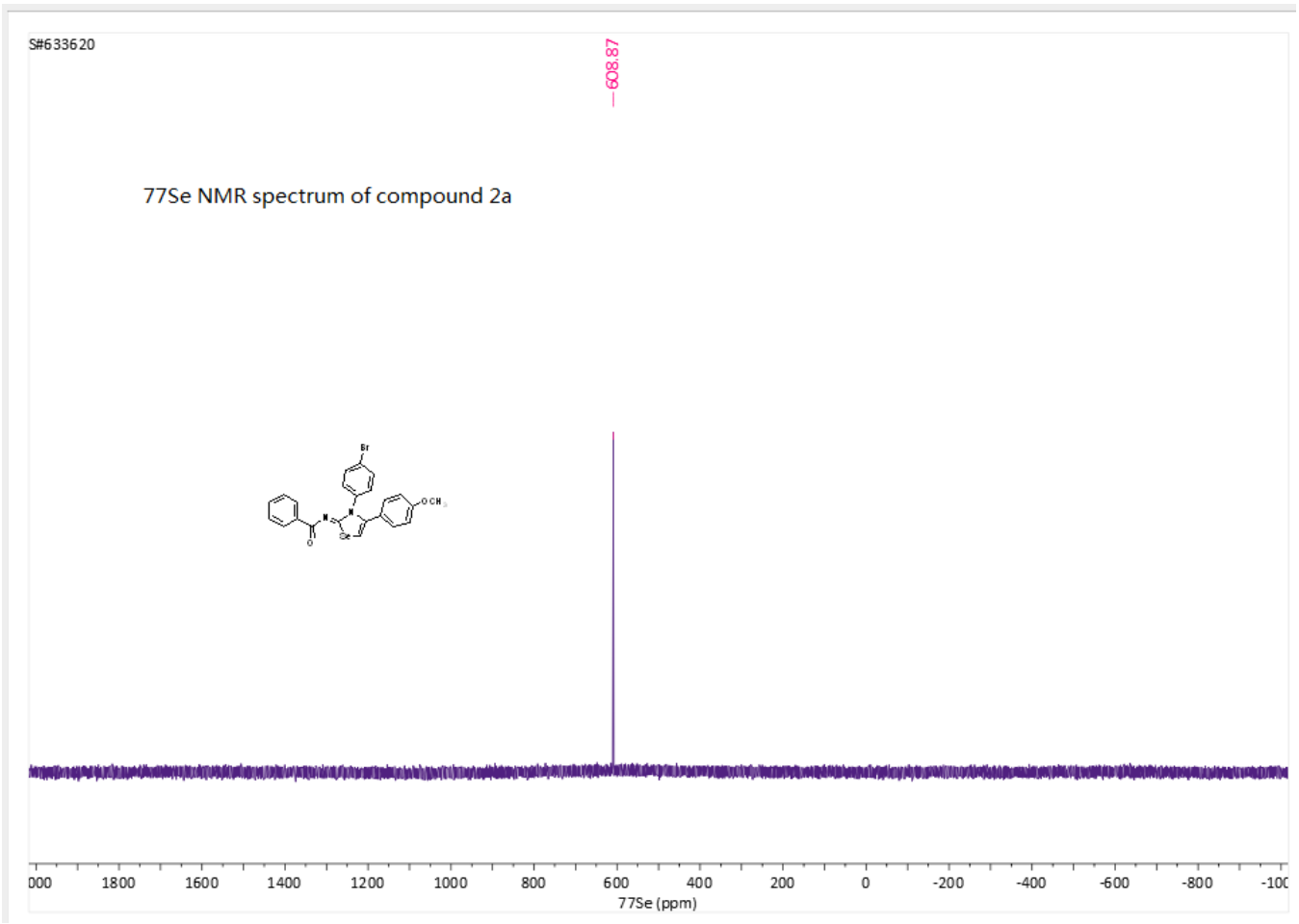


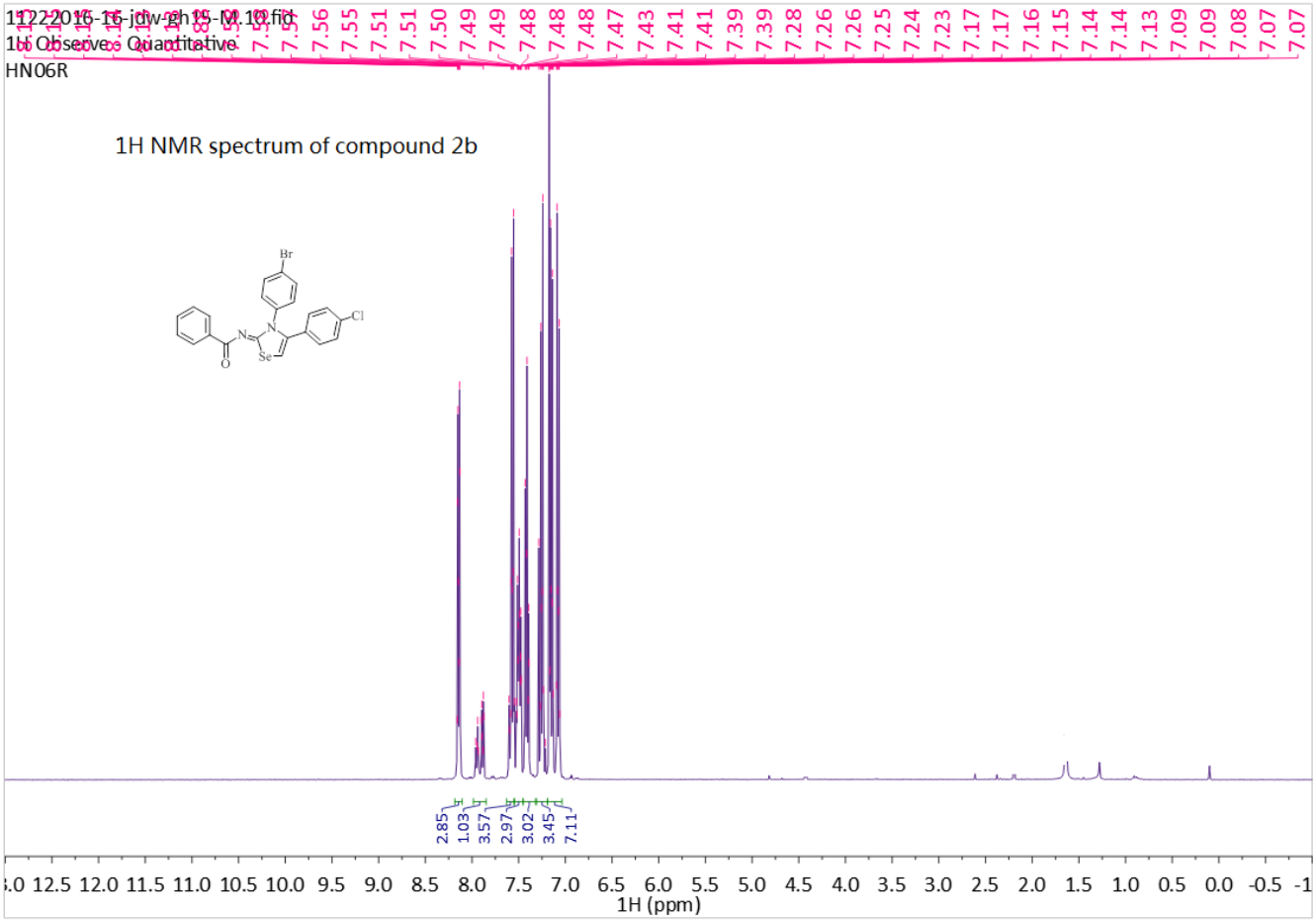

05192014-29-huaR.11.fid
HW402-1
180.64
167.46
143.15
137.83
134.50
132.56
131.49
129.75
128.02
126.62
122.08
121.31
119.32
113.48
77.91 CDCl3
77.48 CDCl3
77.06 CDCl3
13 C NMR spectrum of compound 1
Se
O
Br
N
H
N
H
13C (ppm)

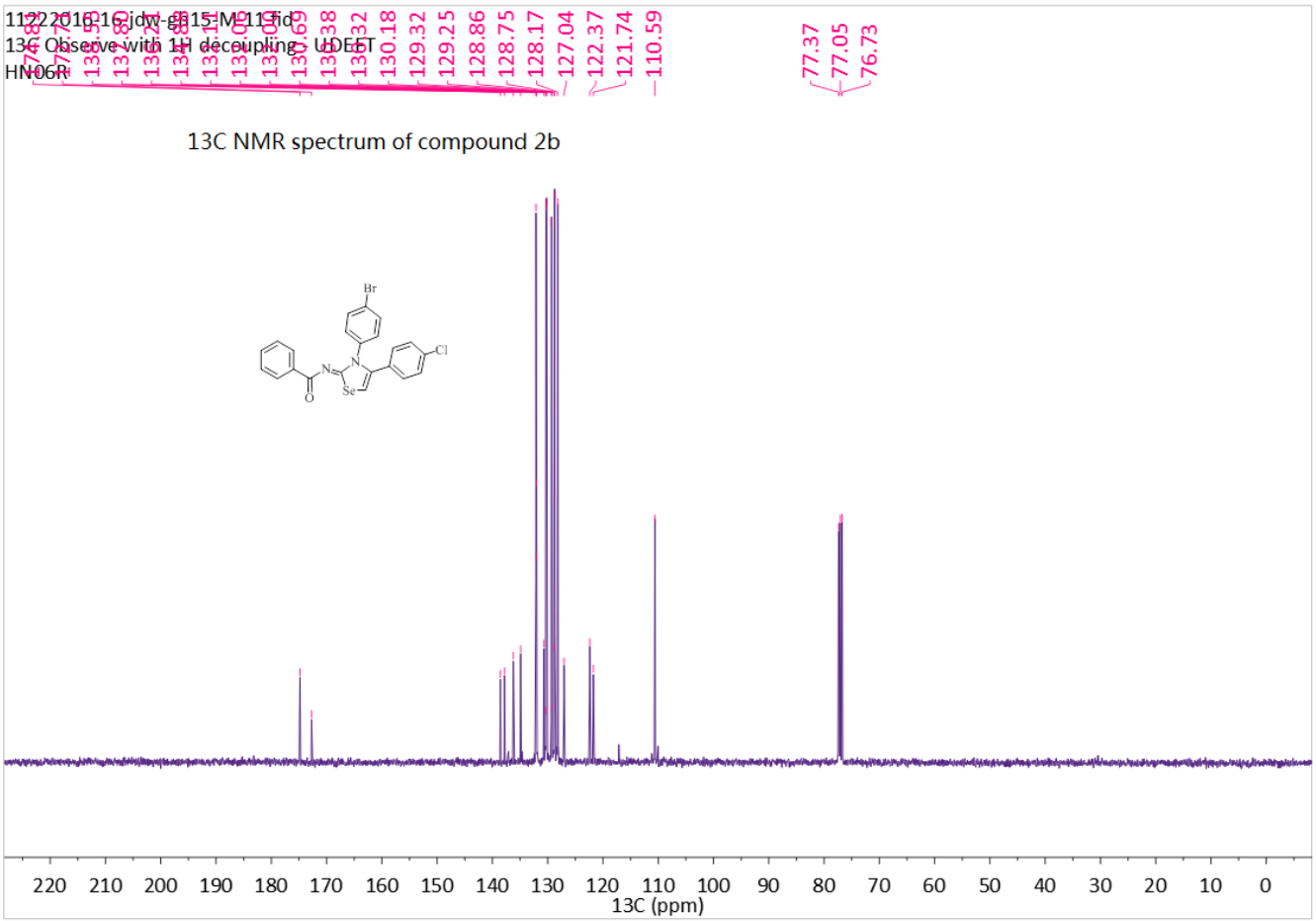

S#643965
419.71
77Se NMR spectrum of compound 1
Br
Se
O
000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-100
77Se (ppm)

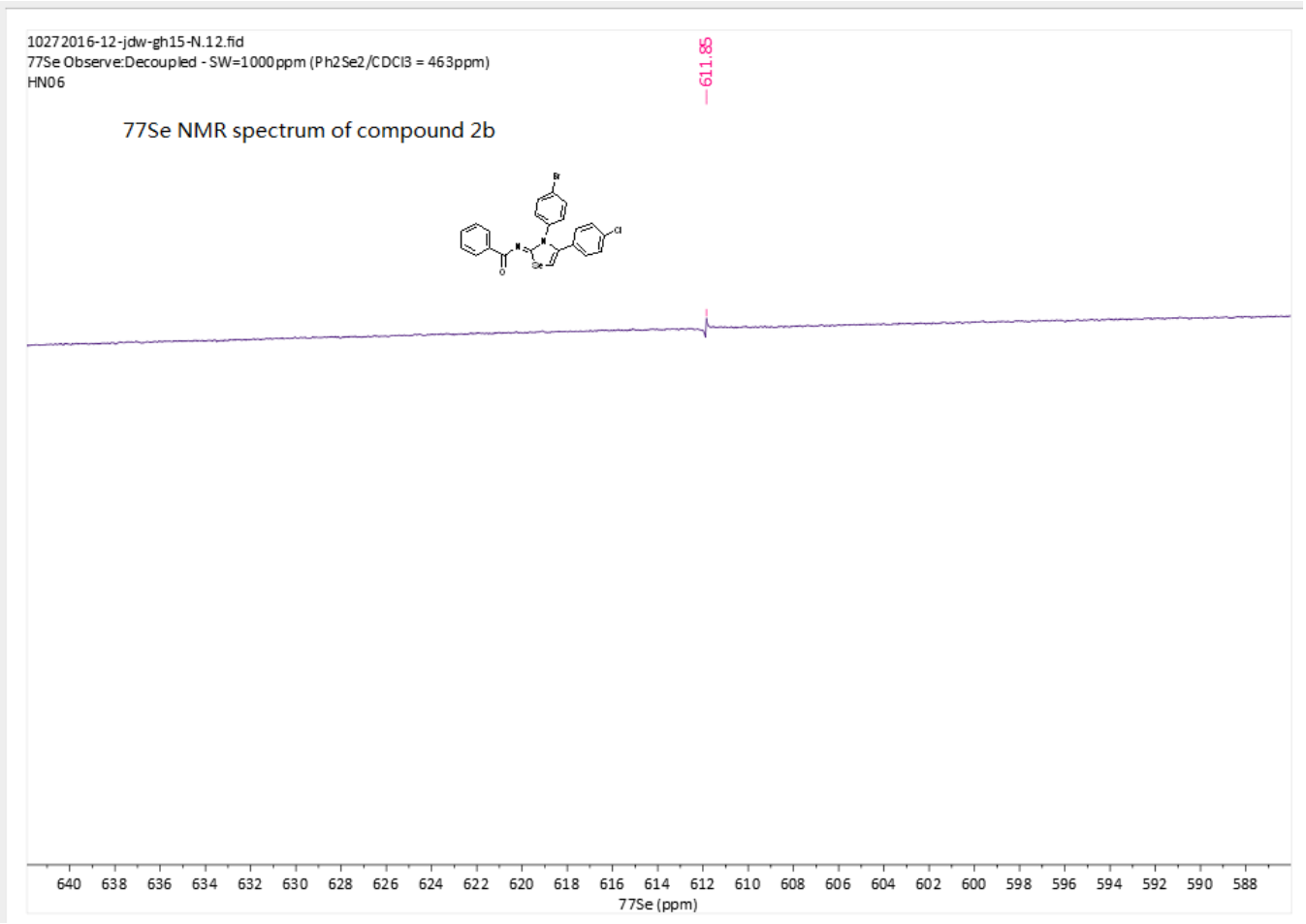

10252015-16-jdw-ch15-M.10.fid
1H Observe Quantitative
HW407rcrstal
1H NMR spectrum of compound 2a
7.58 7.56 7.56 7.55 7.54 7.53 7.52 7.51 7.51 7.50 7.49 7.48 7.48 7.47 7.42 7.41 7.40 7.39 7.38 7.28 7.16 7.16 7.15 7.14 7.10 7.07 7.06 7.05 7.04 6.80 6.79 6.78 6.77 3.81
3.16 1.12 1.76 5.94 0.96 3.24 3.28 4.75 3.18 4.62
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1H (ppm)

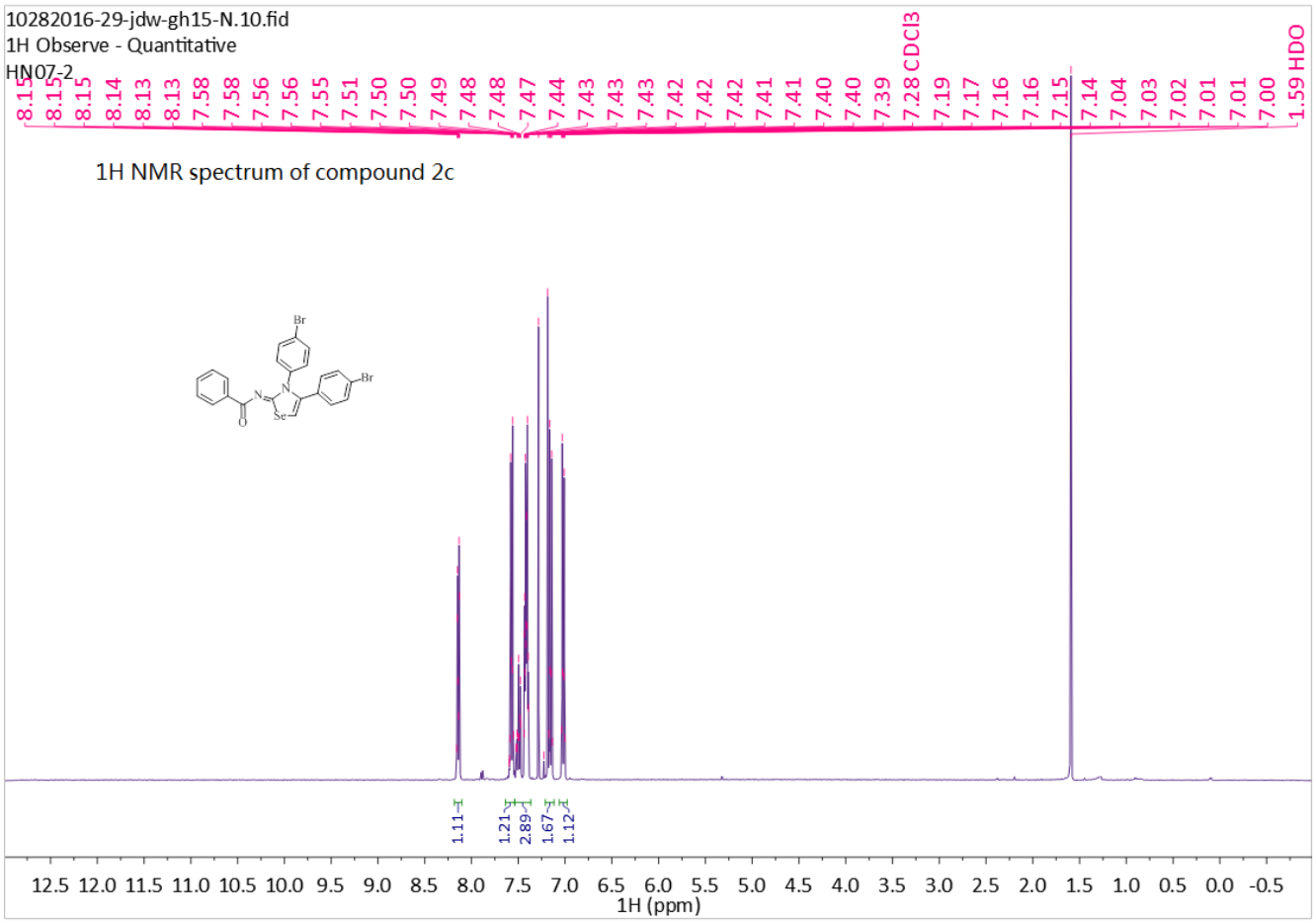

10252016-16-jdw-gh15-M.11.fid
13C Observe with 1H decoupling - UDEFT
HW407rcrstal
177.2
177.5
159.73
139.60
138.16
136.41
134.64
132.06
131.91
131.85
130.49
130.30
129.28
128.86
128.13
127.04
124.51
122.08
121.75
117.13
113.83
109.09
77.37
77.05
76.73
55.28
13C NMR spectrum of compound 2a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)

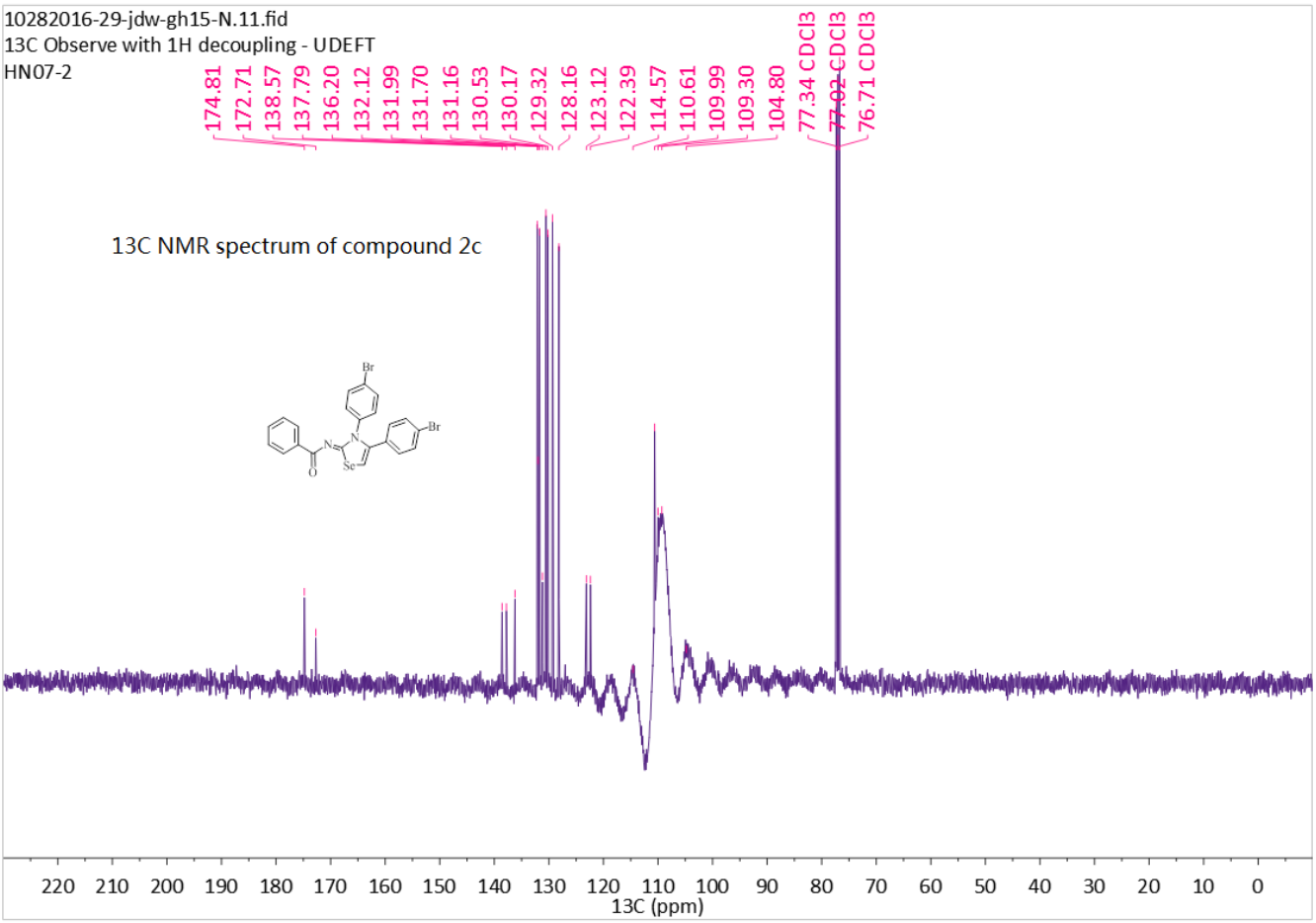

S#633620
608.87
77Se NMR spectrum of compound 2a
Br
O CH3
000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-100
77Se (ppm)

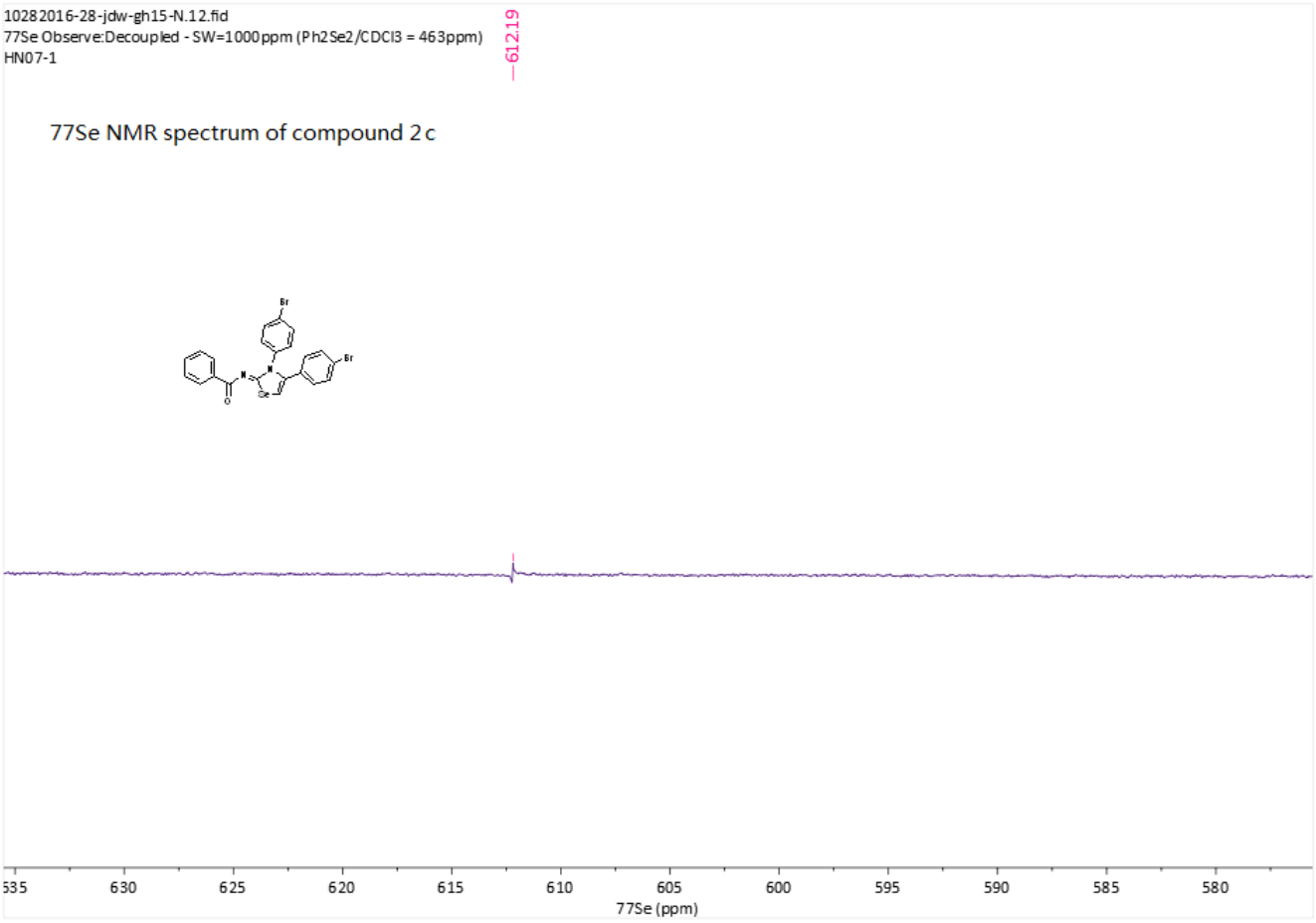

1122-2015-16-jdw-ph15-M.10.fid
1H Observe - Quantitative
HN06R
1H NMR spectrum of compound 2b
Br
Cl
N
Se
O
2.85
1.03
3.57
2.97
3.02
3.45
7.11
1H (ppm)

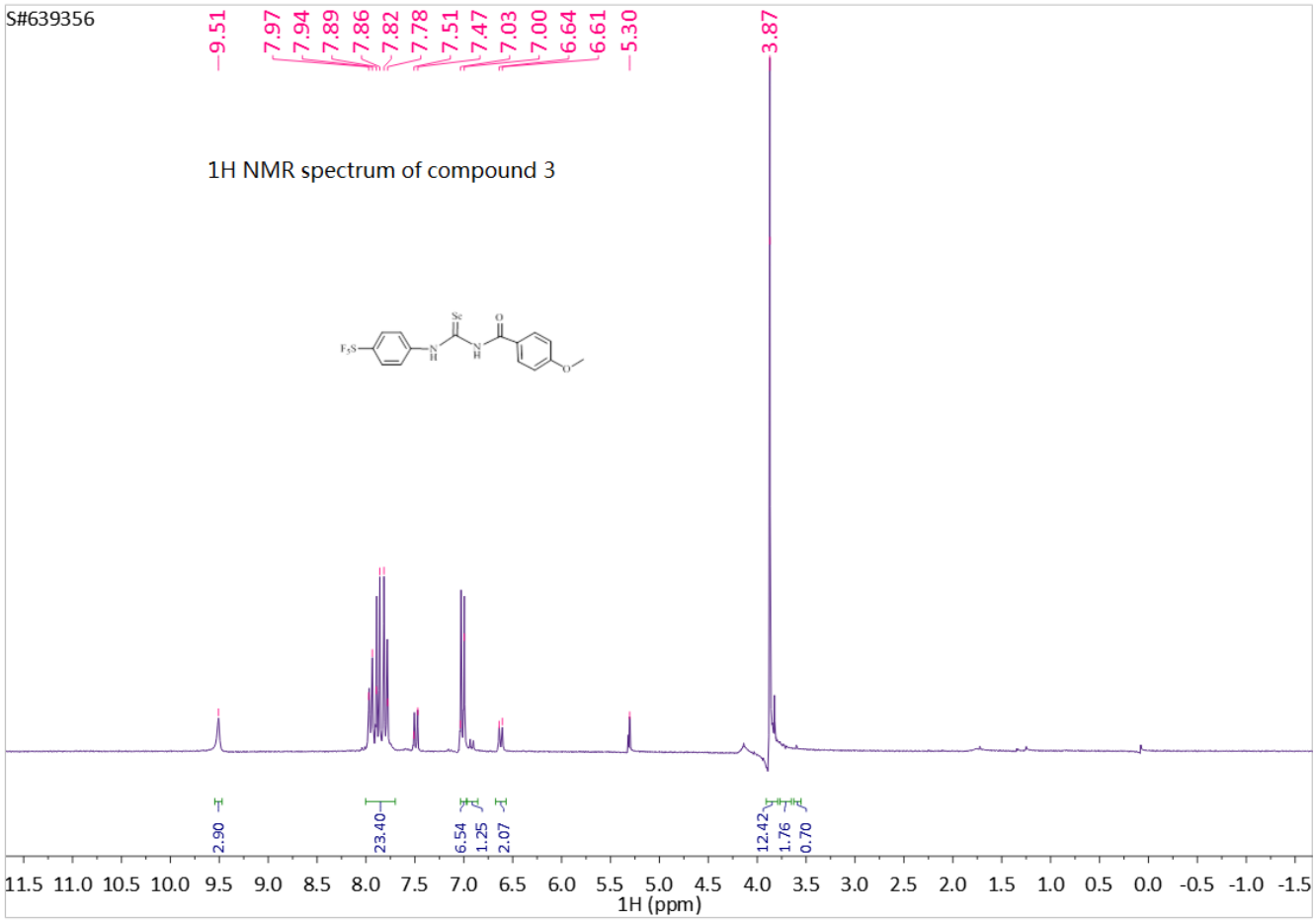

112220161-1c jdw-gb15-M-11 fid
13C Observe with 1H decoupling - UDEFT
HN06R
13C NMR spectrum of compound 2b
Br
Cl
N
Se
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)

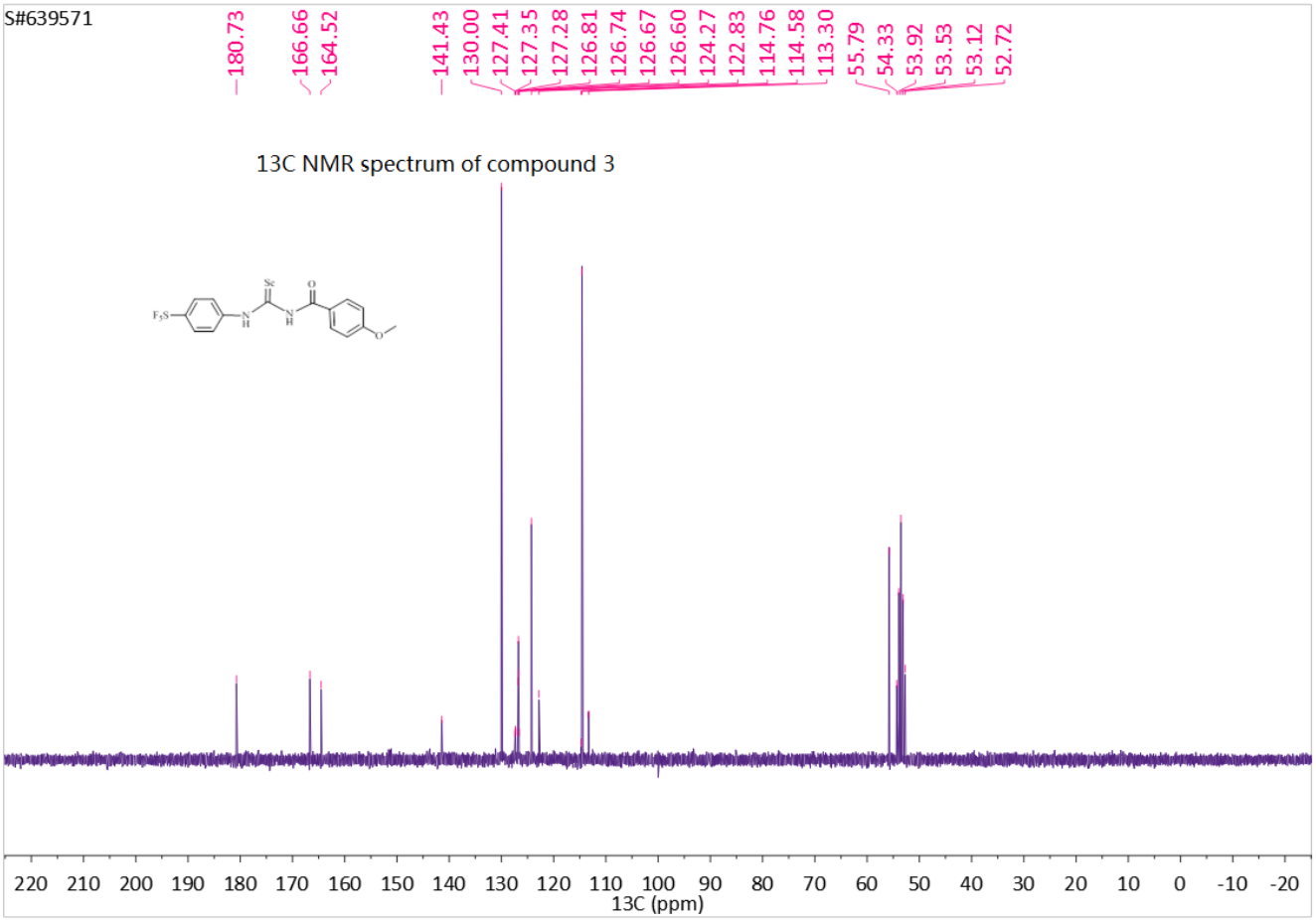

10272016-12-jdw-gh15-N.12.fid
77Se Observe:Decoupled - SW=1000ppm (Ph2Se2/CDCl3 = 463ppm)
HN06
611.85
77Se NMR spectrum of compound 2b
Br
Cl
N
Se
O
640 638 636 634 632 630 628 626 624 622 620 618 616 614 612 610 608 606 604 602 600 598 596 594 592 590 588
77Se (ppm)

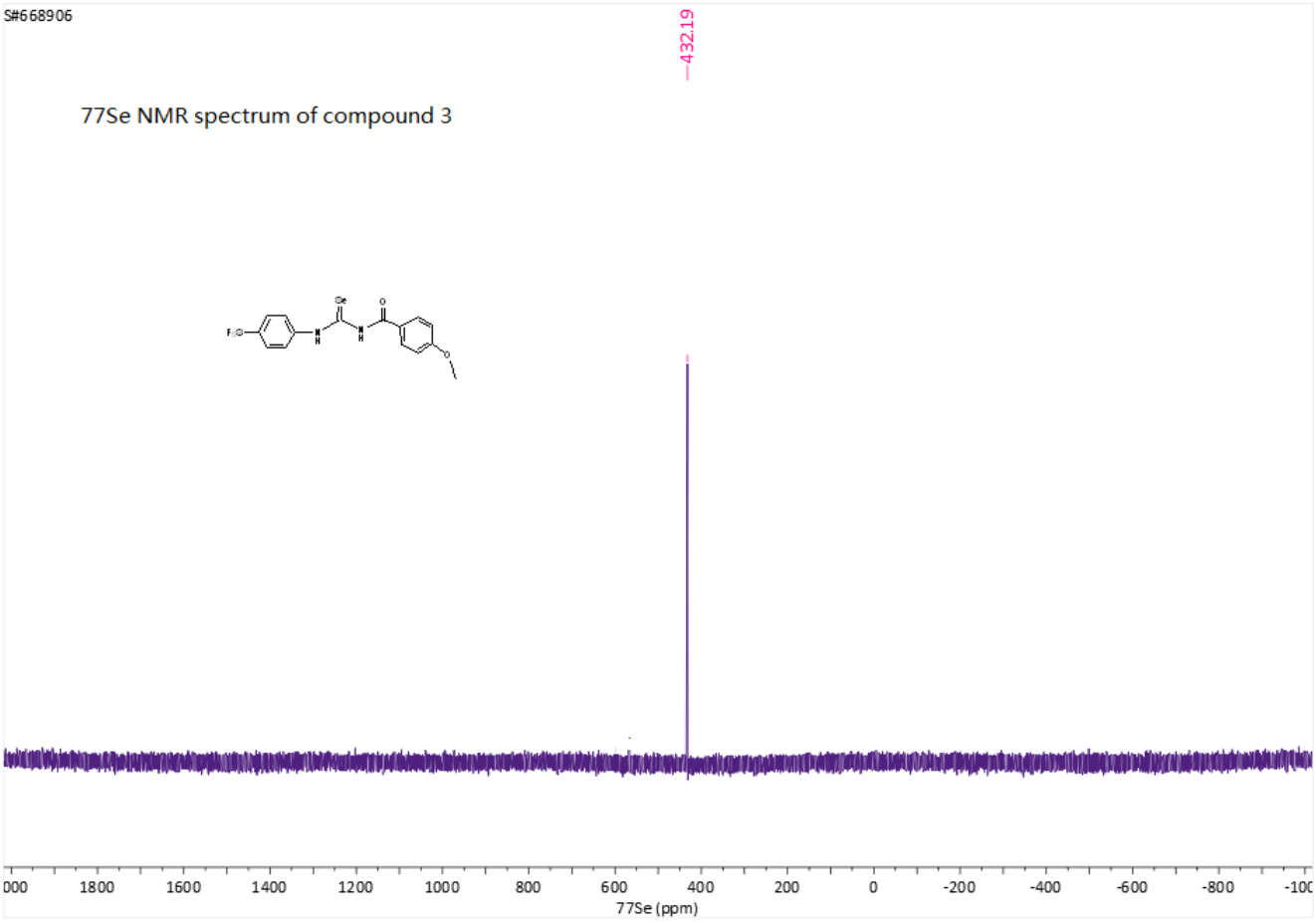

10282016-29-jdw-gh15-N.10.fid
1H Observe - Quantitative
HN07-2
1H NMR spectrum of compound 2c
CDCl3
HDO
1.11
1.21
2.89
1.67
1.12
1H (ppm)

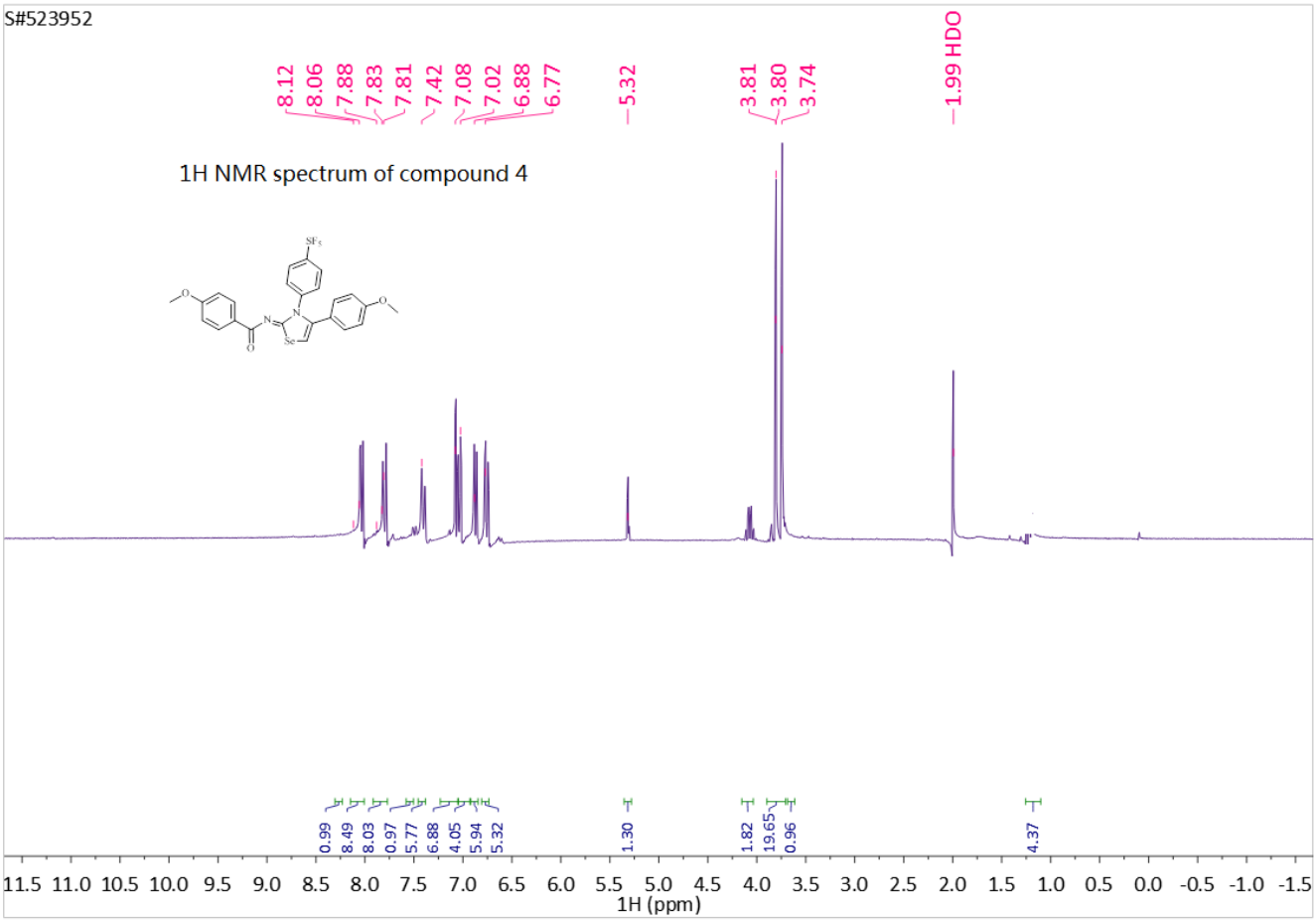

10282016-29-jdw-gh15-N.11.fid
13C Observe with 1H decoupling - UDEFT
HN07-2
174.81
172.71
138.57
137.79
136.20
132.12
131.99
131.70
131.16
130.53
130.17
129.32
128.16
123.12
122.39
114.57
110.61
109.99
109.30
104.80
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
13C NMR spectrum of compound 2c
Br
Br
N
Se
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)

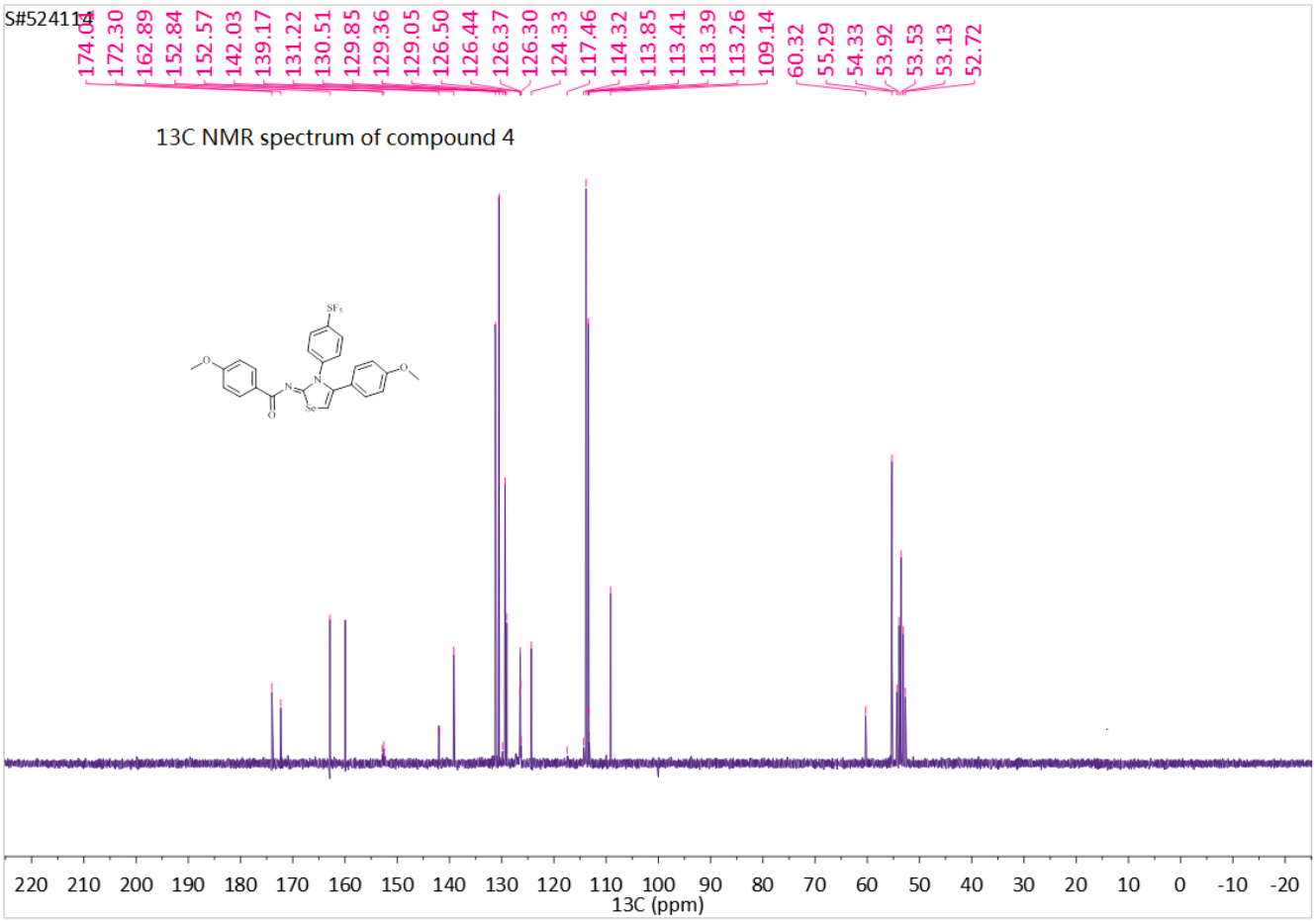

10282016-28-jdw-gh15-N.12.fid
77Se Observe:Decoupled - SW=1000ppm (Ph2Se2/CDCl3 = 463ppm)
HN07-1
612.19
77Se NMR spectrum of compound 2c
Br
Br
535
630
625
620
615
610
605
600
595
590
585
580
77Se (ppm)

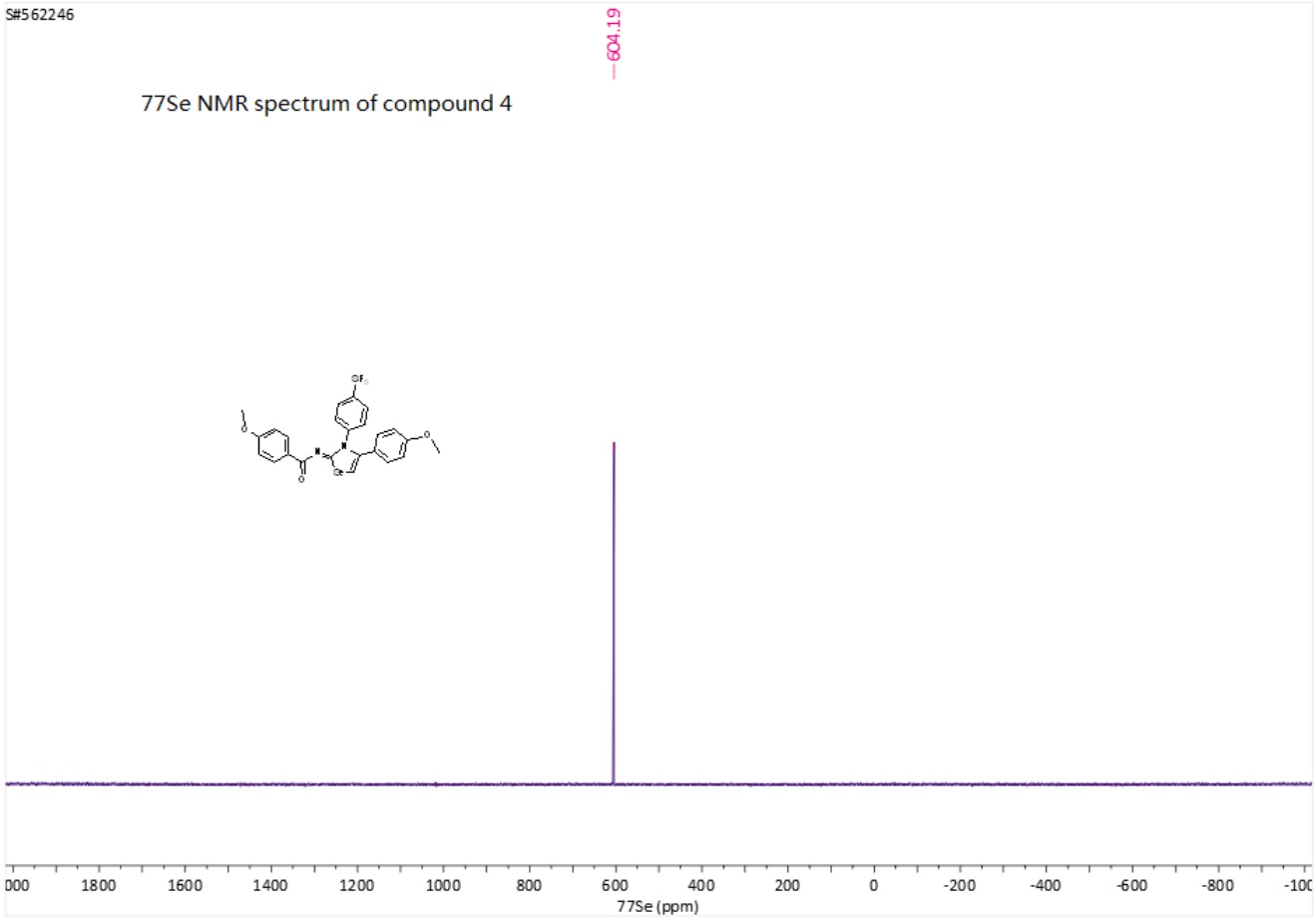

S#639356
9.51
7.97
7.94
7.89
7.86
7.82
7.78
7.51
7.47
7.03
7.00
6.64
6.61
5.30
3.87
1H NMR spectrum of compound 3
2.90
23.40
6.54
1.25
2.07
12.42
1.76
0.70
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
1H (ppm)

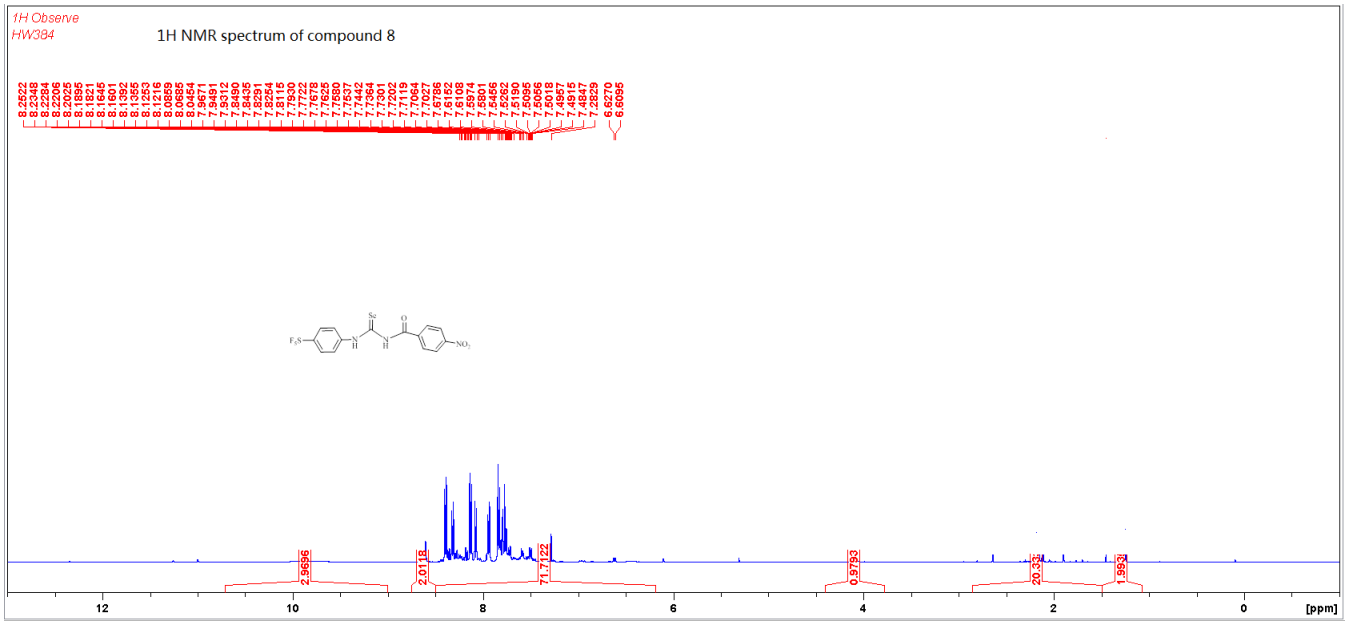

S#639571
180.73
166.66
164.52
141.43
130.00
127.41
127.35
127.28
126.81
126.74
126.67
126.60
124.27
122.83
114.76
114.58
113.30
55.79
54.33
53.92
53.53
53.12
52.72
13C NMR spectrum of compound 3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
13C (ppm)

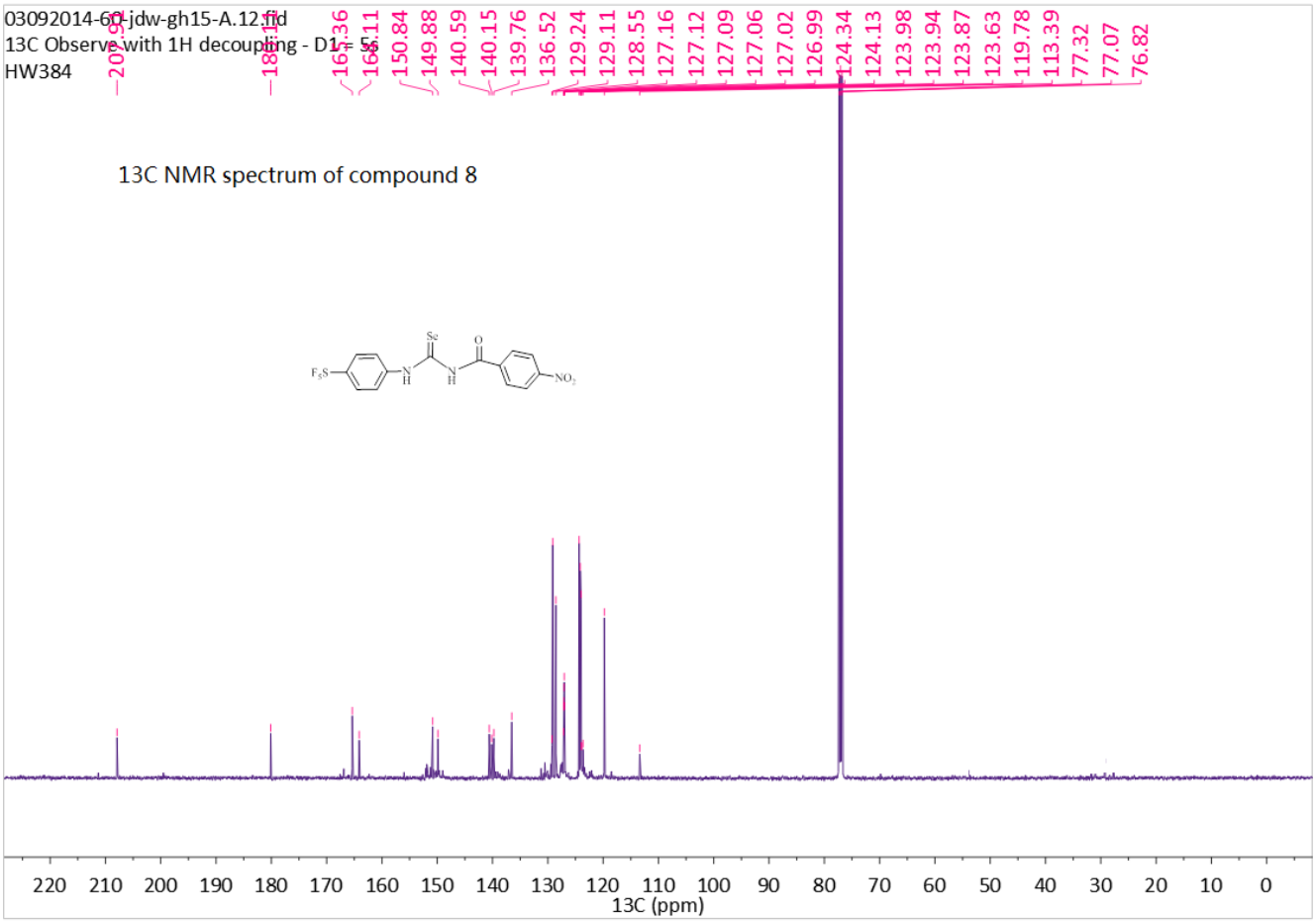

S#668906
432.19
77Se NMR spectrum of compound 3
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
77Se (ppm)

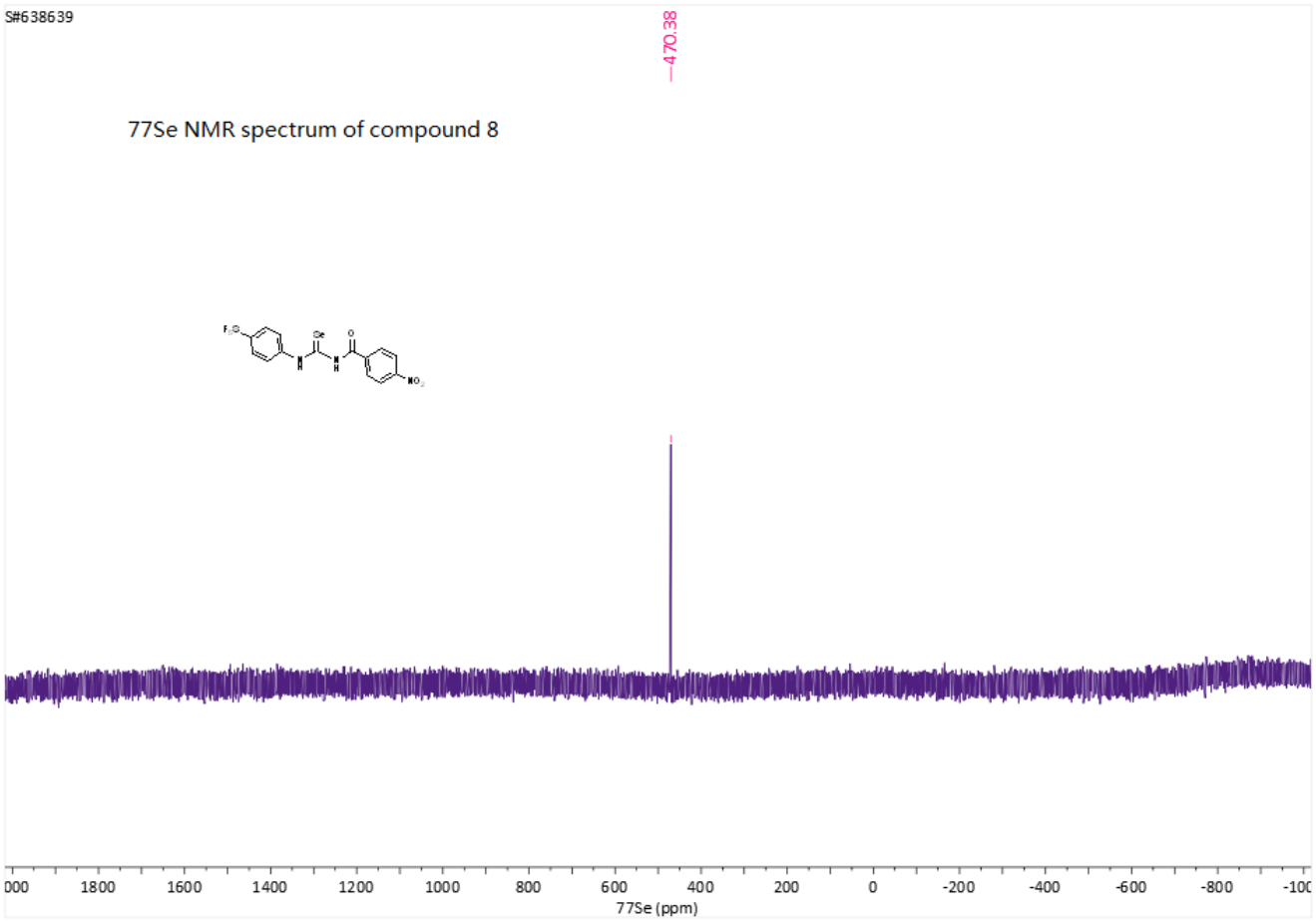

S#523952
8.12
8.06
7.88
7.83
7.81
7.42
7.08
7.02
6.88
6.77
5.32
3.81
3.80
3.74
1.99 HDO
1H NMR spectrum of compound 4
0.99
8.49
8.03
0.97
5.77
6.88
4.05
5.94
5.32
1.30
1.82
19.65
0.96
4.37
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
1H (ppm)

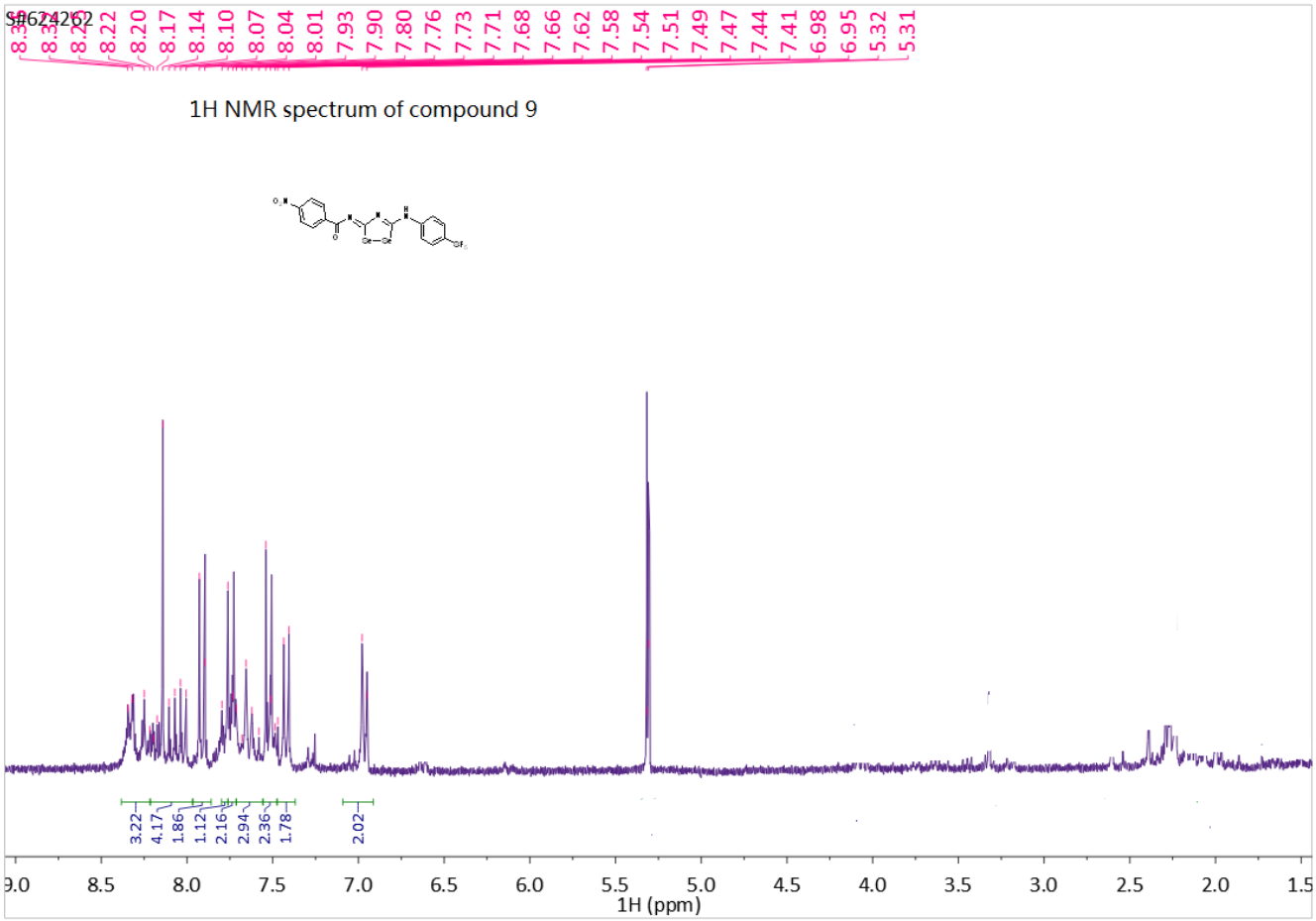

S#524114
174.04
172.30
162.89
152.84
152.57
142.03
139.17
131.22
130.51
129.85
129.36
129.05
126.50
126.44
126.37
126.30
124.33
117.46
114.32
113.85
113.41
113.39
113.26
109.14
60.32
55.29
54.33
53.92
53.53
53.13
52.72
13C NMR spectrum of compound 4
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
13C (ppm)

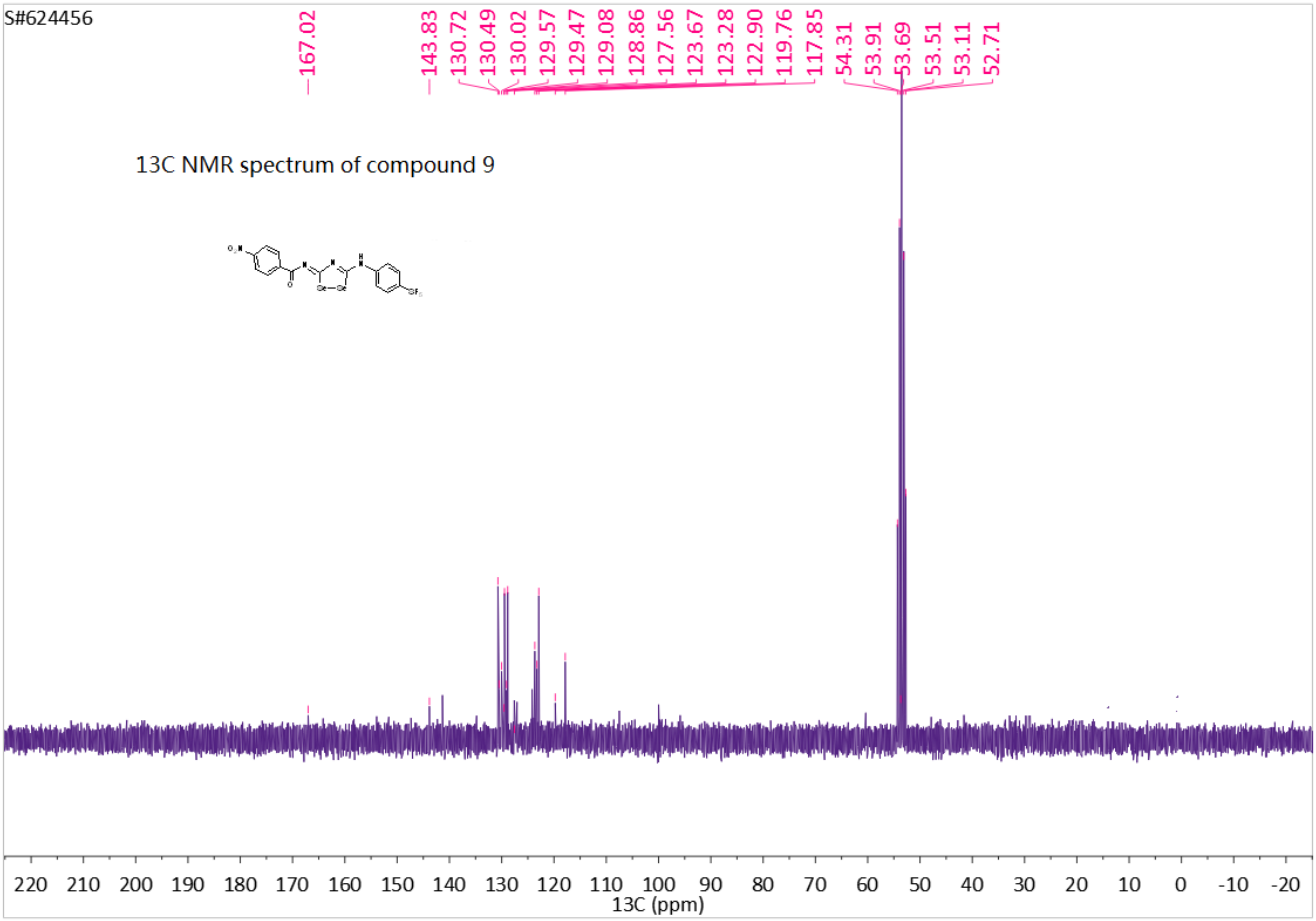

S#562246
604.19
77Se NMR spectrum of compound 4
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
77Se (ppm)

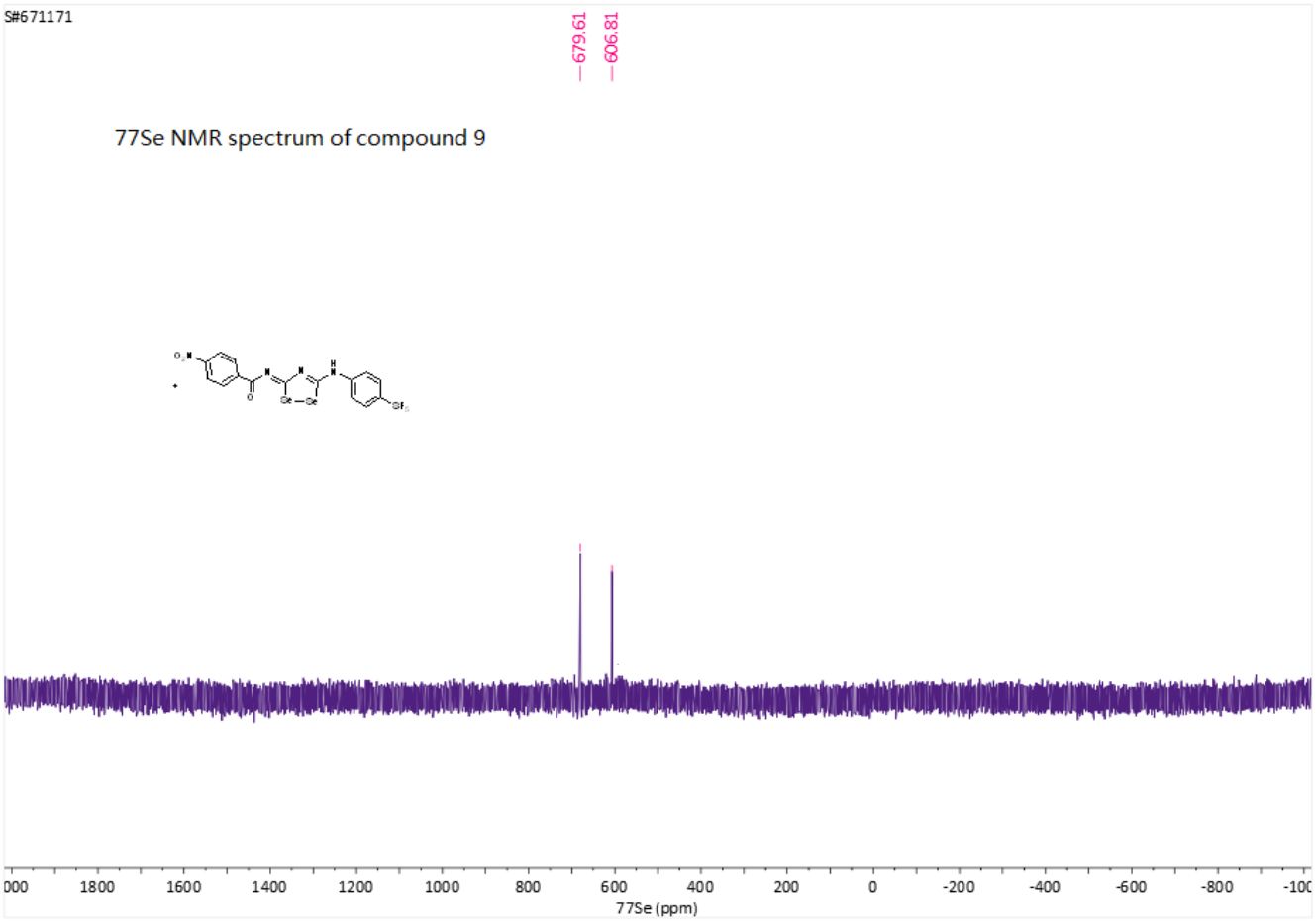

1H Observe
HW384
1H NMR spectrum of compound 8
2.9696
2.0118
7.1722
0.9793
20.3
1.9934
12
10
8
6
4
2
0
[ppm]

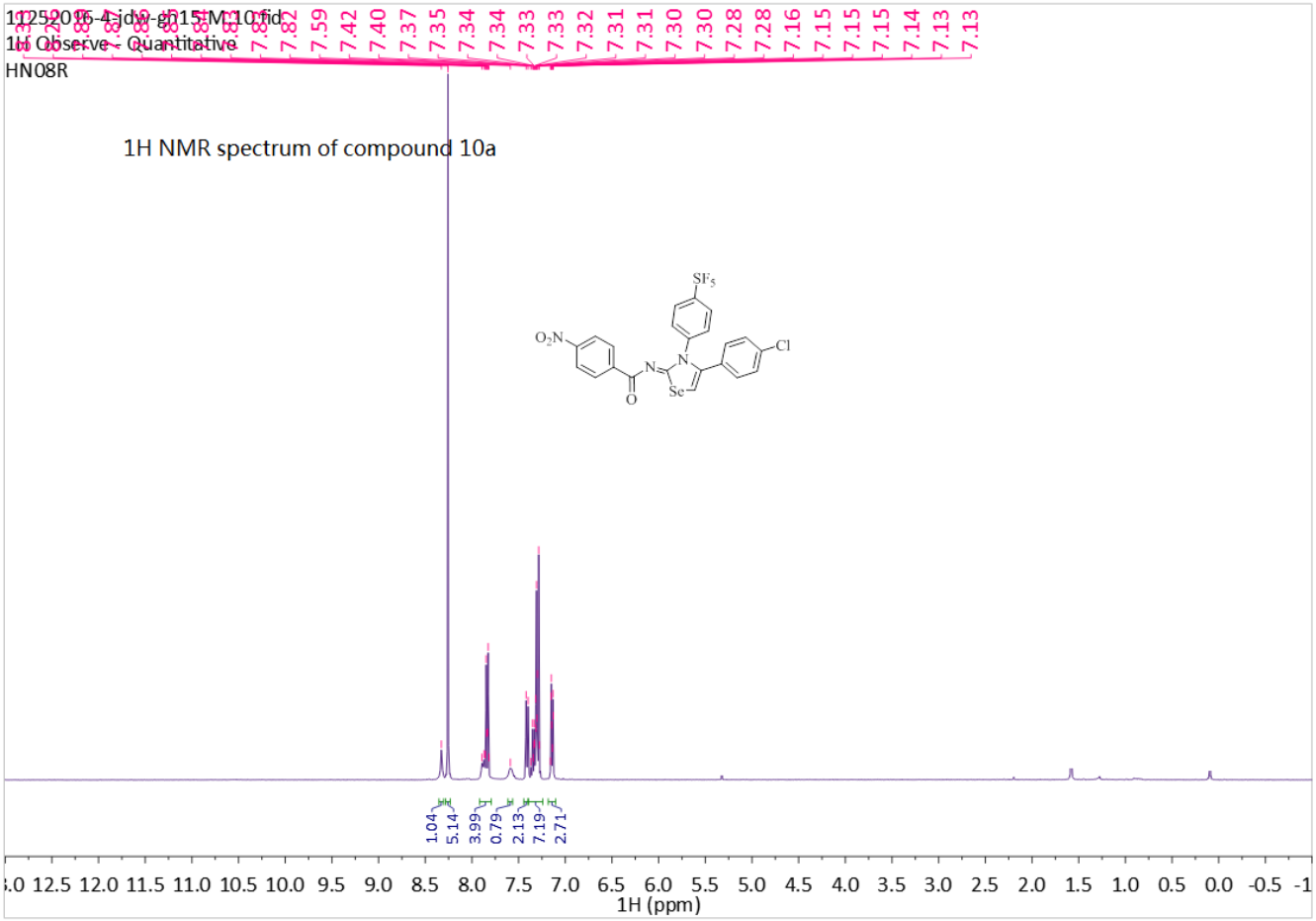

03092014-60-jdw-gh15-A.12.fid
13C Observe with 1H decoupling - D1 = 5s
HW384
13C NMR spectrum of compound 8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)

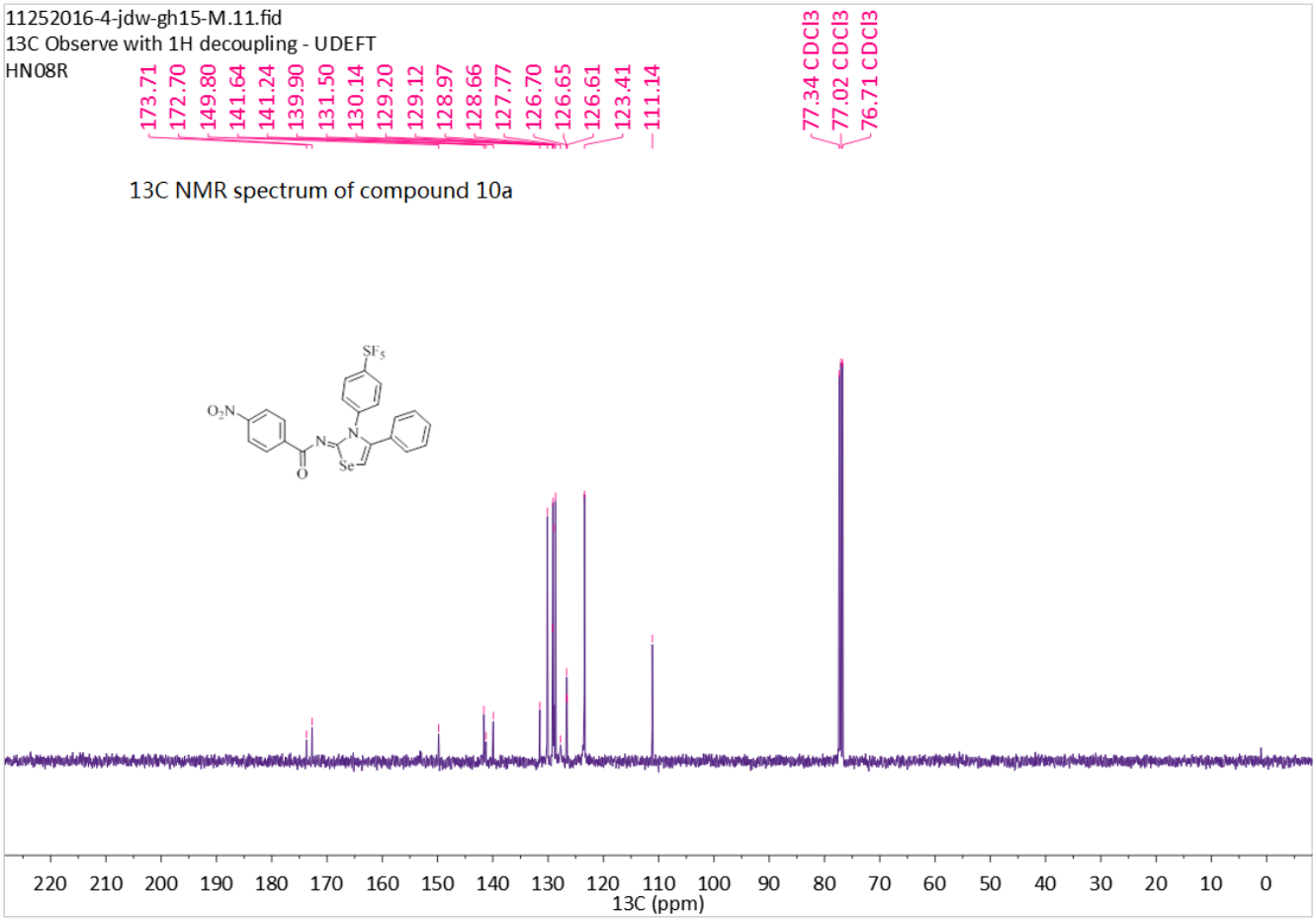

S#638639
470.38
77Se NMR spectrum of compound 8
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
77Se (ppm)

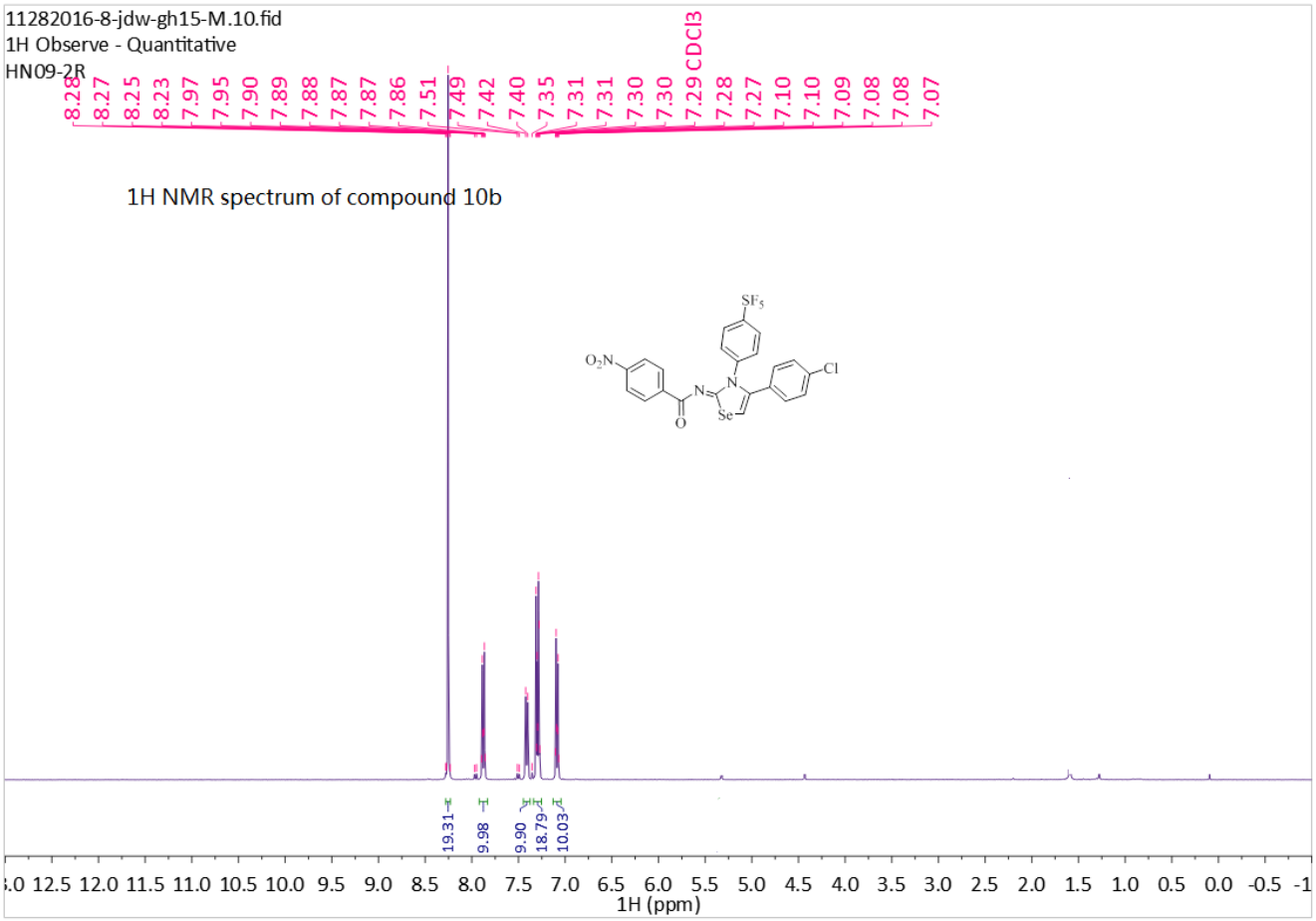

SH6242G2
8.34 8.32 8.22 8.20 8.17 8.14 8.10 8.07 8.04 8.01 7.93 7.90 7.80 7.76 7.73 7.71 7.68 7.66 7.62 7.58 7.54 7.51 7.49 7.47 7.44 7.41 6.98 6.95 5.32 5.31
1H NMR spectrum of compound 9
3.22 4.17 1.86 1.12 2.16 2.94 2.36 1.78 2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
1H (ppm)

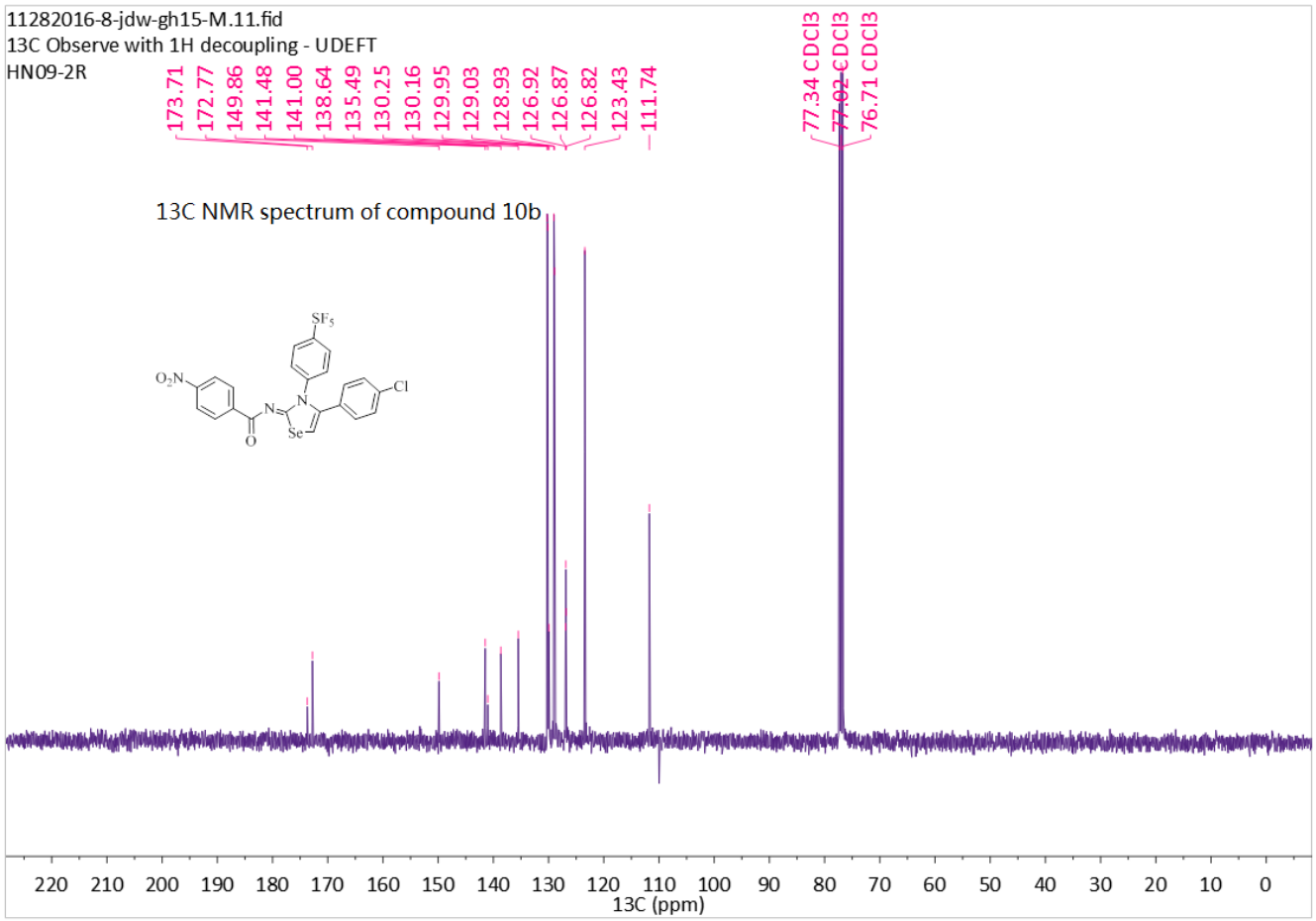

S#624456
167.02
143.83
130.72
130.49
130.02
129.57
129.47
129.08
128.86
127.56
123.67
123.28
122.90
119.76
117.85
54.31
53.91
53.69
53.51
53.11
52.71
13C NMR spectrum of compound 9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
13C (ppm)

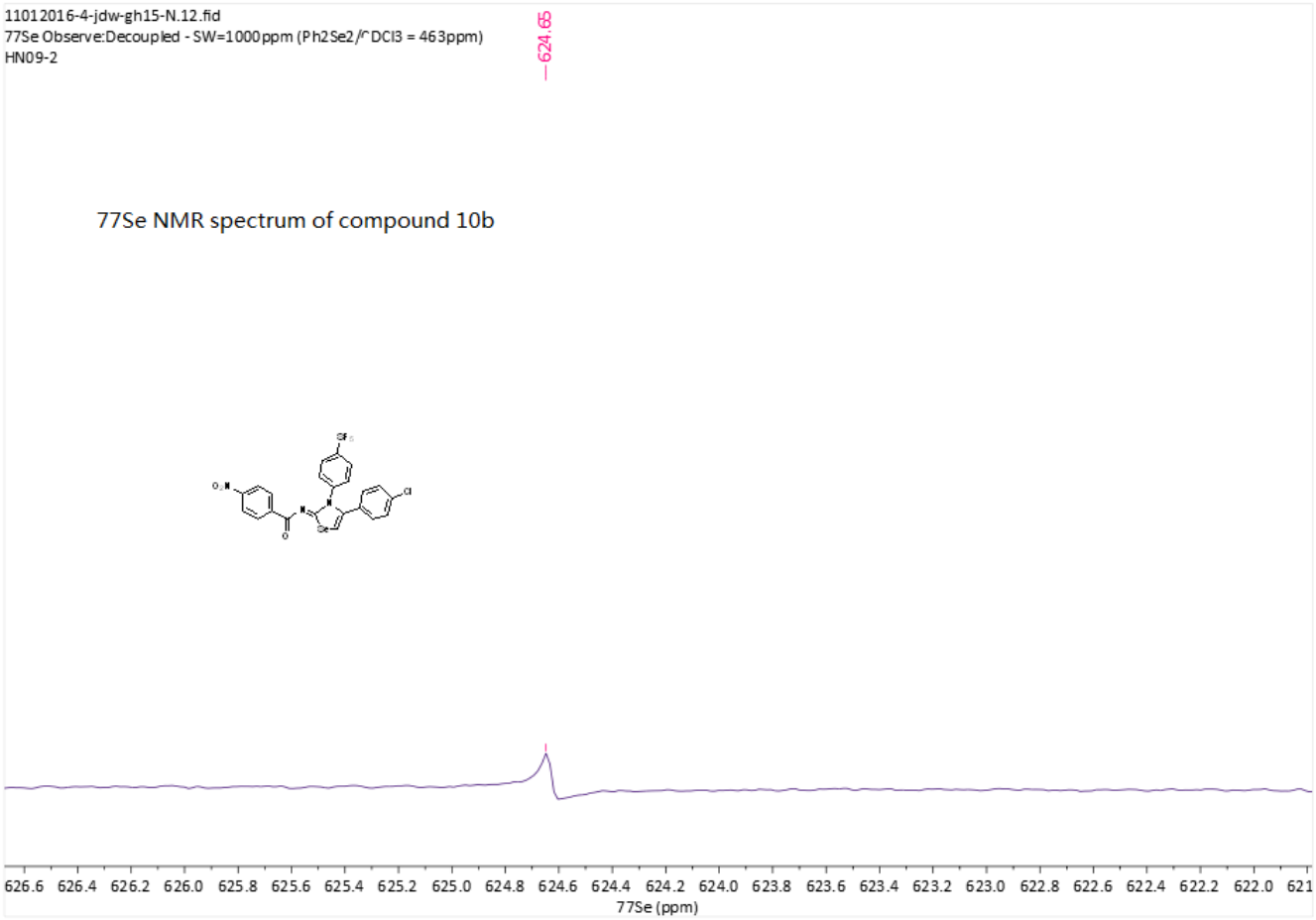

S#671171
679.61
606.81
77Se NMR spectrum of compound 9
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
77Se (ppm)

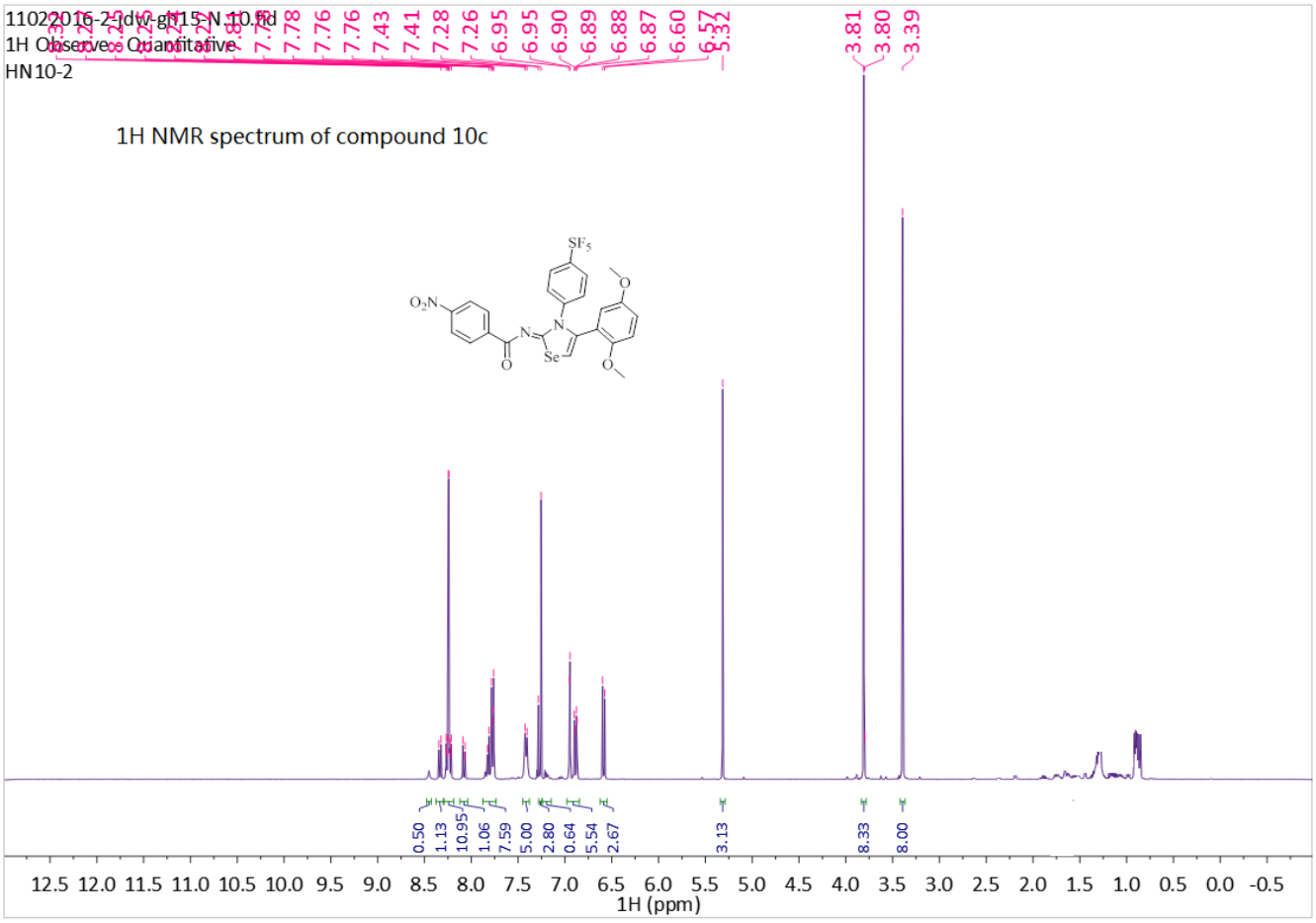

1125201 6-4-jdw-p15-M-10-fid
1H Observe - Quantitative
HN08R
1H NMR spectrum of compound 10a
1.04
5.14
3.99
0.79
2.13
7.19
2.71
1H (ppm)

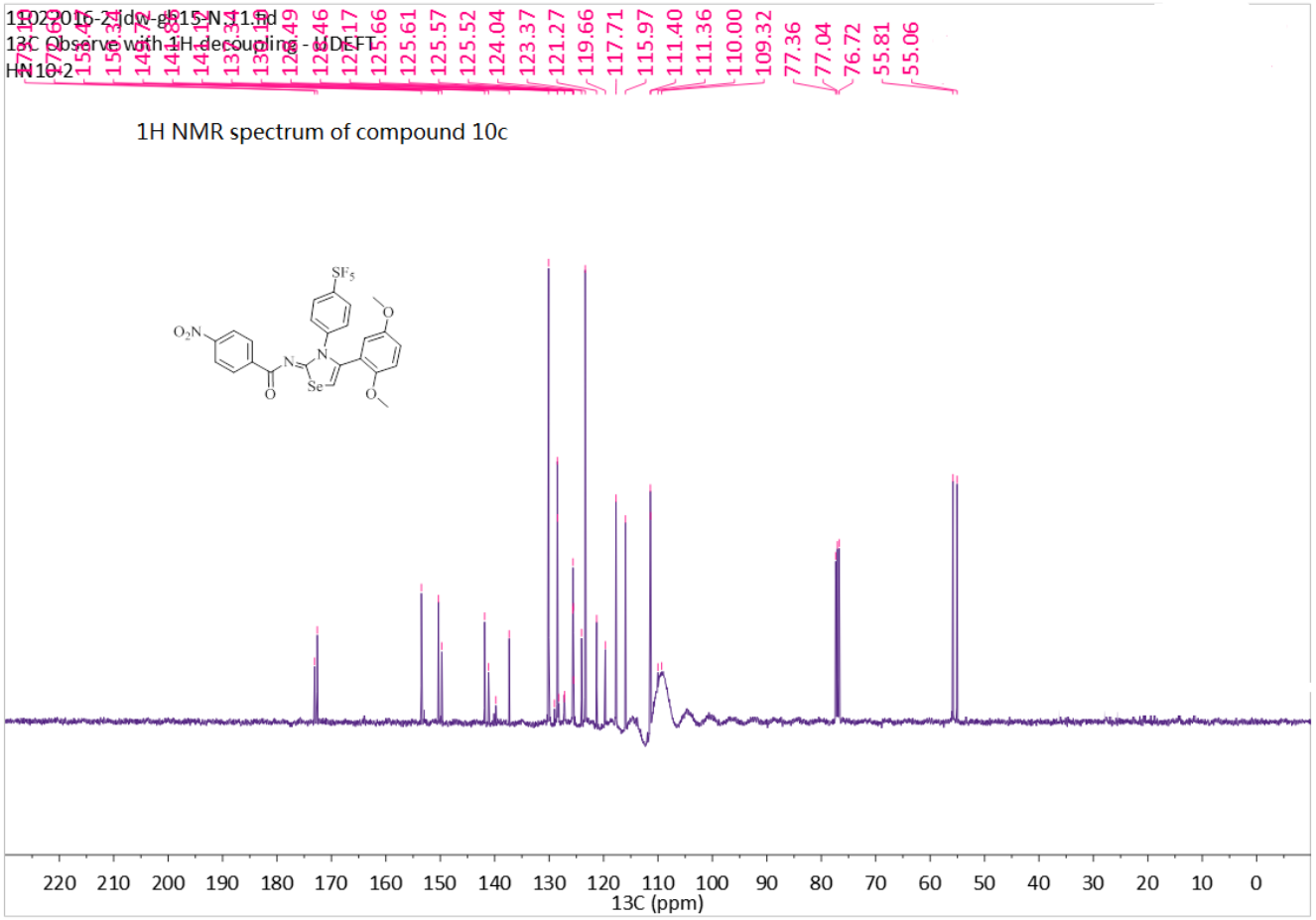

11252016-4-jdw-gh15-M.11.fid
13C Observe with 1H decoupling - UDEFT
HN08R
173.71
172.70
149.80
141.64
141.24
139.90
131.50
130.14
129.20
129.12
128.97
128.66
127.77
126.70
126.65
126.61
123.41
111.14
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
13C NMR spectrum of compound 10a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)

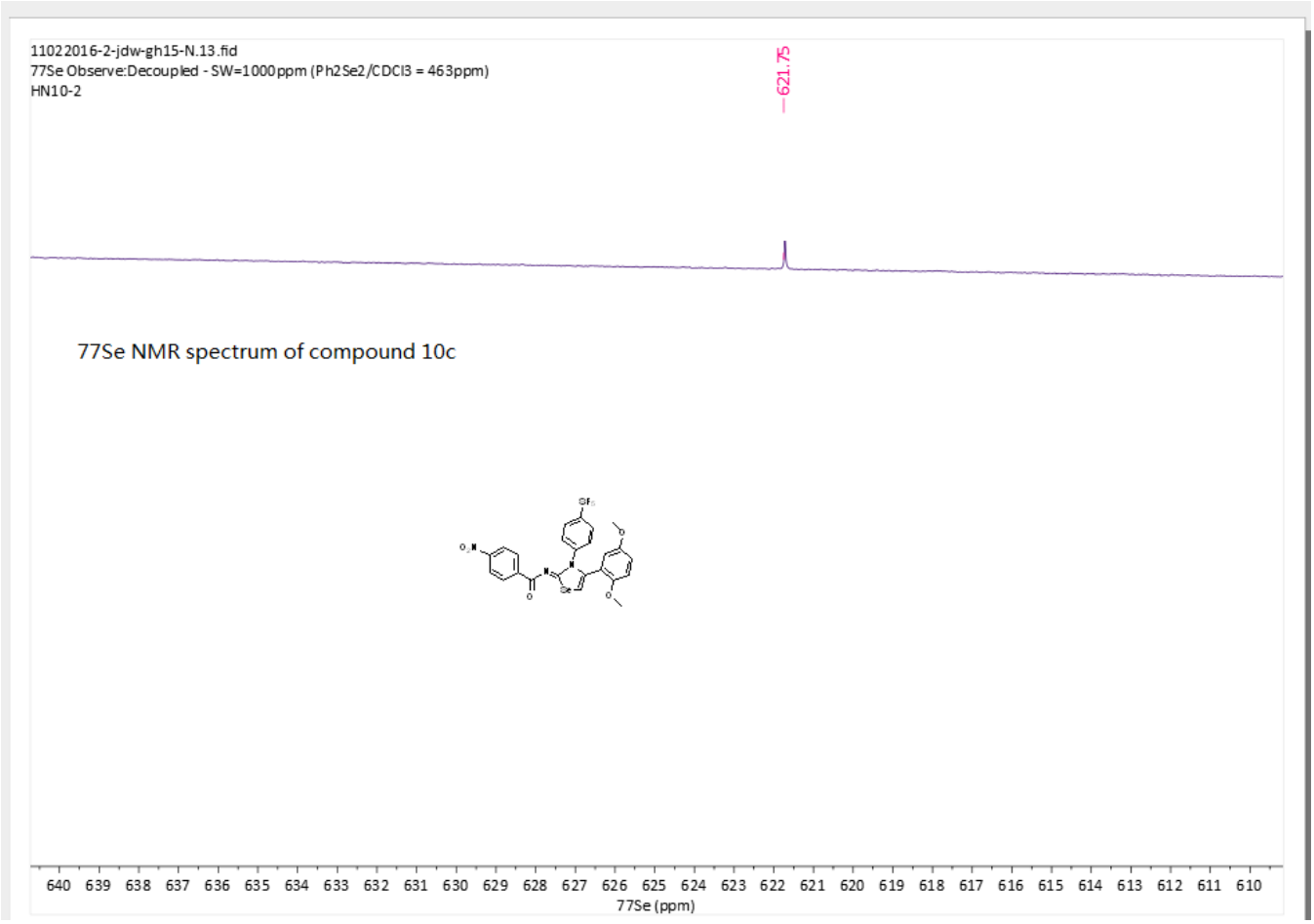

11282016-8-jdw-gh15-M.10.fid
1H Observe - Quantitative
HN09-2R
8.28 8.27 8.25 8.23 7.97 7.95 7.90 7.89 7.88 7.87 7.87 7.86 7.51 7.49 7.42 7.40 7.35 7.31 7.31 7.30 7.30 7.29 CDCl3 7.28 7.27 7.10 7.10 7.09 7.08 7.08 7.07
1H NMR spectrum of compound 10b
SF5
O2N
N
Cl
Se
O
19.31
9.98
9.90
18.79
10.03
1H (ppm)


11282016-8-jdw-gh15-M.11.fid
13C Observe with 1H decoupling - UDEFT
HN09-2R
173.71
172.77
149.86
141.48
141.00
138.64
135.49
130.25
130.16
129.95
129.03
128.93
126.92
126.87
126.82
123.43
111.74
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
13C NMR spectrum of compound 10b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)

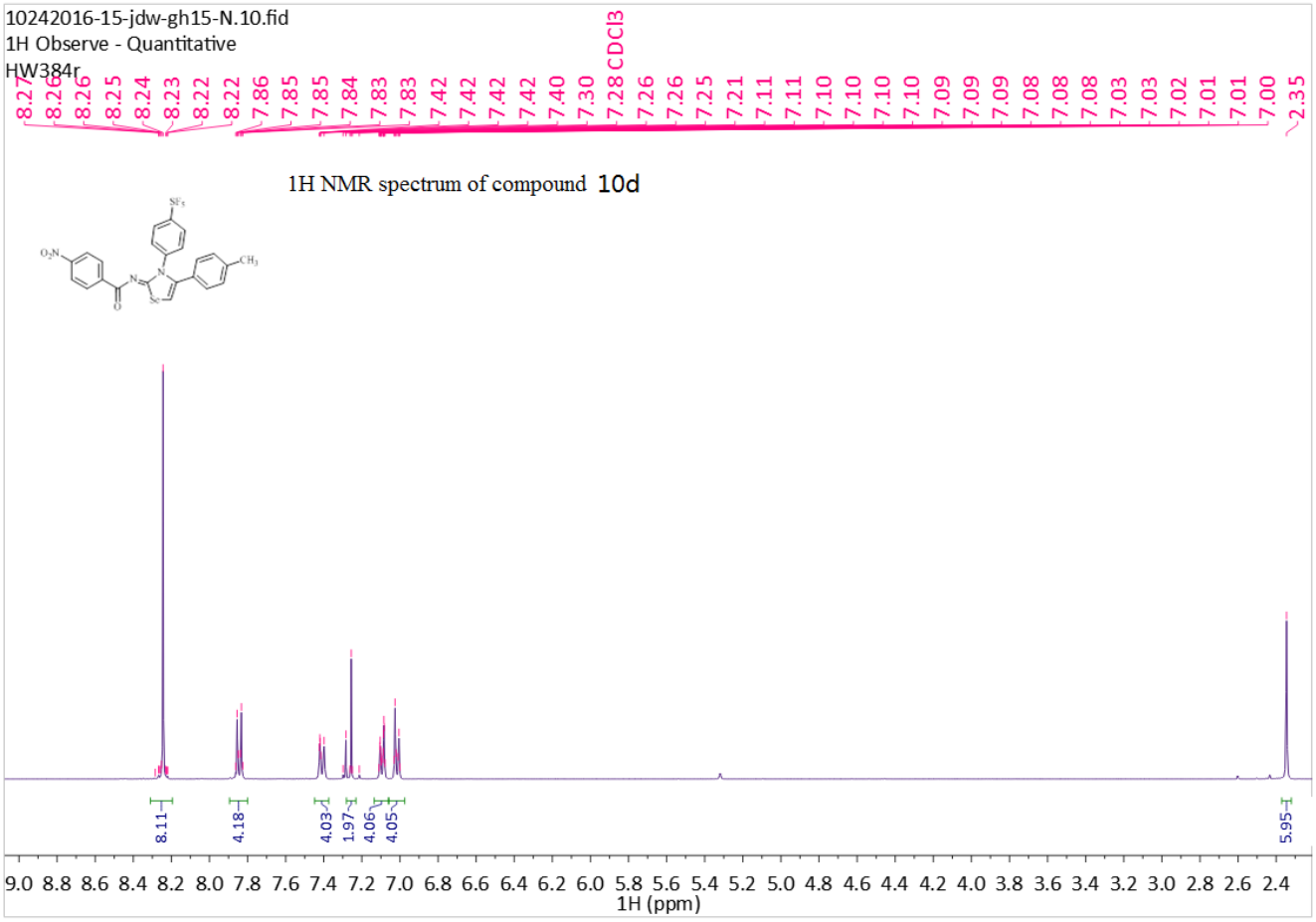

11012016-4-jdw-gh15-N.12.fid
77Se Observe:Decoupled - SW=1000ppm (Ph2Se2/~DCl3 = 463ppm)
HN09-2
624.65
77Se NMR spectrum of compound 10b
626.6 626.4 626.2 626.0 625.8 625.6 625.4 625.2 625.0 624.8 624.6 624.4 624.2 624.0 623.8 623.6 623.4 623.2 623.0 622.8 622.6 622.4 622.2 622.0 621
77Se (ppm)

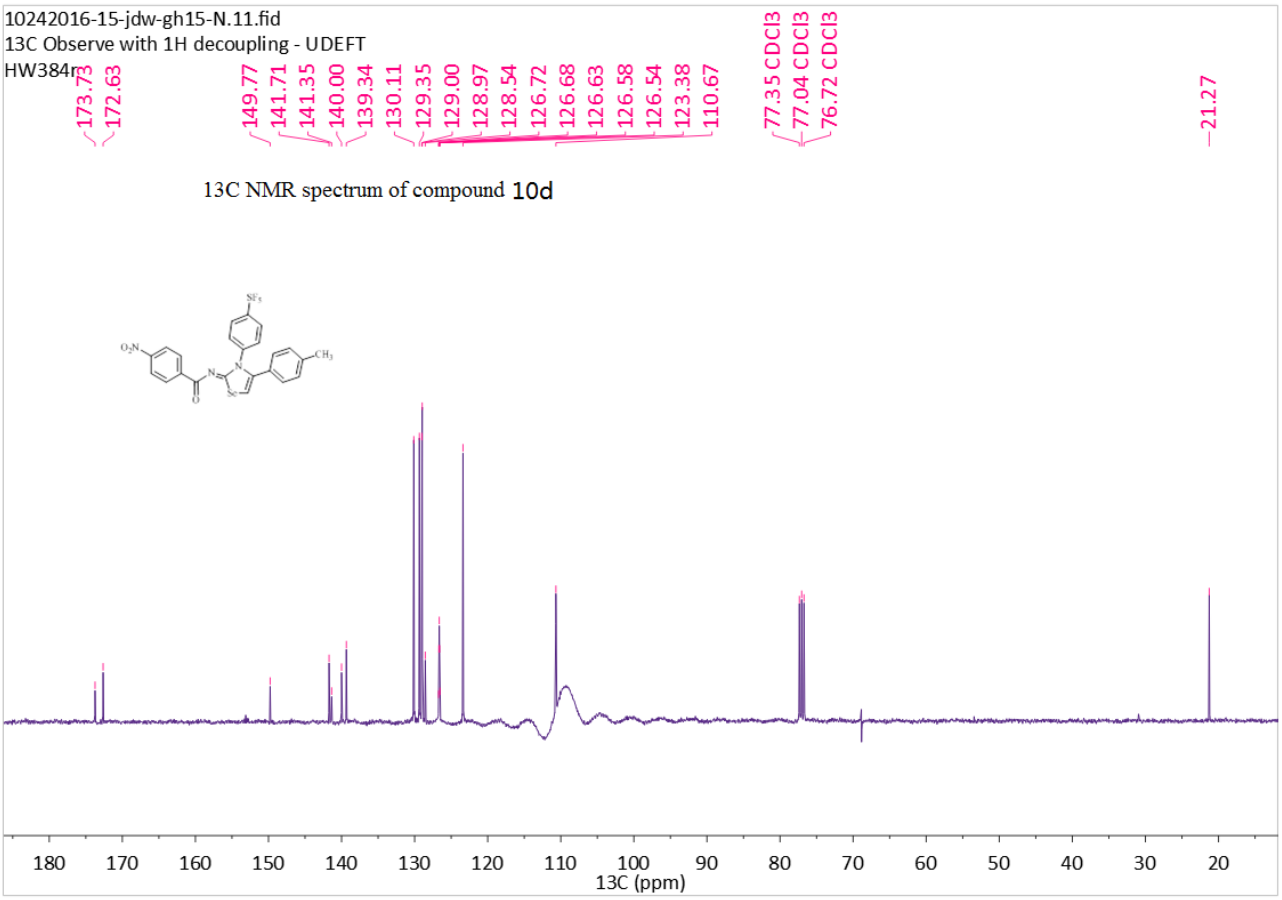

11022016-2-1dw-gH15-N-10.fid
1H Observe Quantitative
HN10-2
1H NMR spectrum of compound 10c
7.78
7.76
7.76
7.43
7.41
7.28
7.26
6.95
6.95
6.90
6.89
6.88
6.87
6.60
6.57
5.32
3.81
3.80
3.39
0.50
1.13
10.95
1.06
7.59
5.00
2.80
0.64
5.54
2.67
3.13
8.33
8.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
1H (ppm)

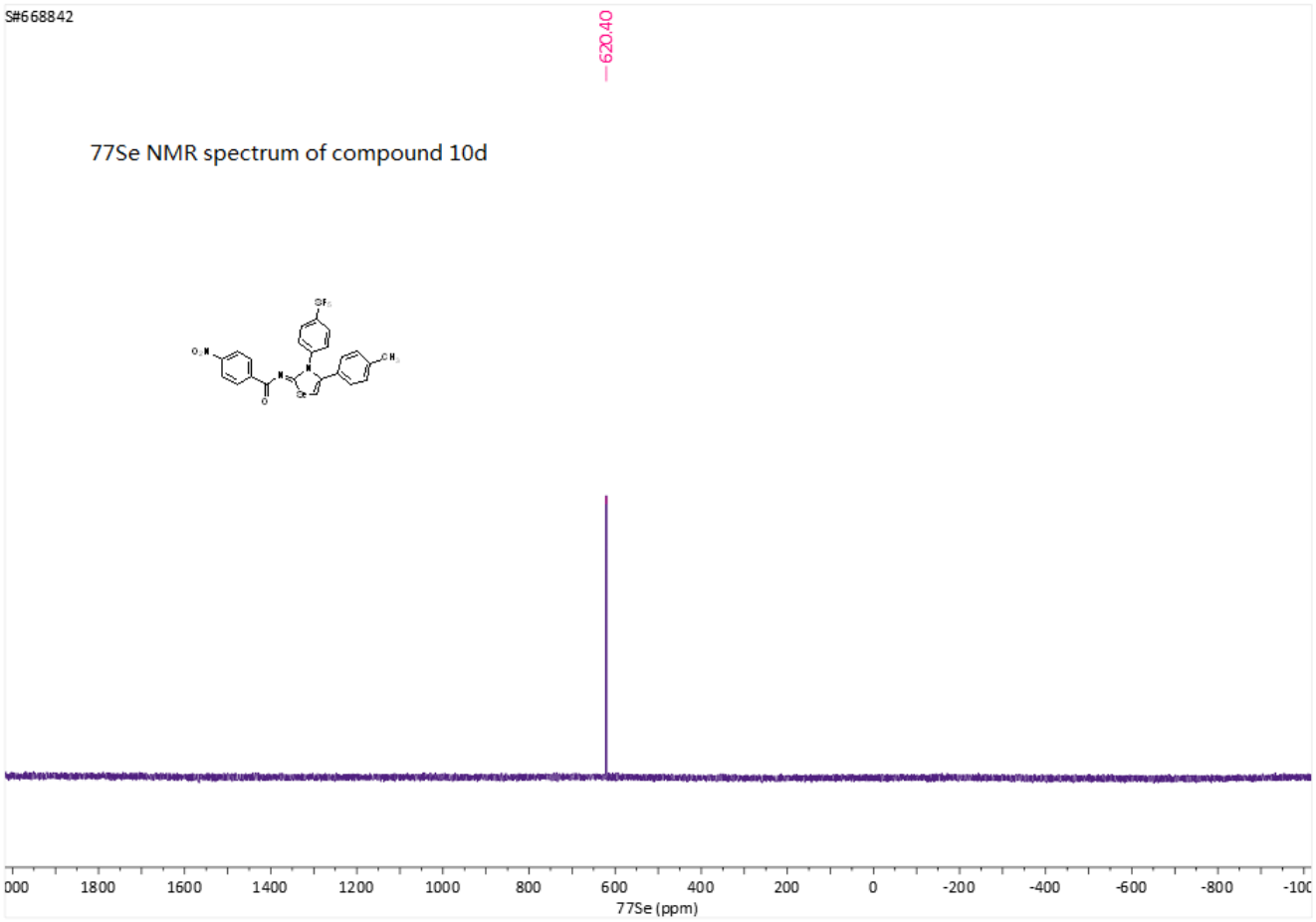

11022016-2-jdw-gb15-N-11.fid
13C Observe with 1H decoupling - JDEFT
HN10-2
1H NMR spectrum of compound 10c
SF5
O2N
O
N
N
Se
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)



77Se NMR spectrum of compound 10c


10242016-15-jdw-gh15-N.10.fid
1H Observe - Quantitative
HW384r
1H NMR spectrum of compound 10d
8.11
4.18
4.03
1.97
4.06
4.05
5.95
1H (ppm)


10242016-15-jdw-gh15-N.11.fid
13C Observe with 1H decoupling - UDEFT
HW384r
173.73
172.63
149.77
141.71
141.35
140.00
139.34
130.11
129.35
129.00
128.97
128.54
126.72
126.68
126.63
126.58
126.54
123.38
110.67
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
21.27
13C NMR spectrum of compound 10d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
13C (ppm)


S#668842
620.40
77Se NMR spectrum of compound 10d
000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
77Se (ppm)

2.

Details of the x-ray data collections and refinements for compounds 2a, 2b, 2c and 3, 4, 6, 7, 9, 10a, 10b, 10c and 10d

Table S1. Details of the x-ray data collections and refinements for compounds **2a**, **2b**, **2c** and **3**

Compound	**2a**	**2b**	**2c**	**3**
Formula	$C_{23}H_{17}BrN_2O_2Se$	$C_{22}H_{14}BrClN_2OSe$	$C_{22}H_{14}Br_2N_2OSe$	$C_{15}H_{13}F_5N_2O_2SSe$
M	512.26	516.68	561.13	459.29
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	9.5971(6)	11.3066(7)	11.3990(7)	17.4151(11)
b/Å	10.5881(7)	11.8464(8)	11.8584(8)	6.5384(5)
c/Å	11.4042(7)	15.0693(10)	15.0948(10)	15.8481(11)
A	65.702(6)	90	90	90
B	79.265(6)	93.197(7)	93.183(6)	109.850(3)
Γ	87.524(7)	90	90	90
U/A^3	1036.98(13)	2015.3(2)	2037.3(2)	1697.4(2)
Z	2	4	4	4
μ/cm^{-1}	37.65	40.00	57.93	24.00
Reflections collected	8657	17162	17055	11794
Independent reflections	3657	3680	3688	3064
R_{int}	0.0995	0.0646	0.1577	0.0782
R1	0.0303	0.0255	0.0389	0.0413
wR2 [$I > 2\sigma(I)$]	0.0845	0.0642	0.1021	0.1012

Table S2. Details of the x-ray data collections and refinements for compounds **4**, **6**, **7** and **9**

Compound	**4**	**6**	**7**	**9**
Formula	$C_{24.5}H_{20}ClF_5N_2O_3SSe$	$C_{10}H_{11}BrN_2$	$C_{12}H_{14}BrN$	$C_{15}H_9F_5N_4O_3SSe_2$
M	631.90	239.11	252.15	578.23
Crystal system	triclinic	orthorhombic	monoclinic	triclinic
Space group	*P*-1	$P2_12_12_1$	$P2_1/c$	*P*-1
a/Å	9.4893(8)	6.1222(10)	7.9086(12)	7.680(4)
b/Å	10.2641(9)	11.956(2)	17.787(3)	10.671(10)
c/Å	13.4203(11)	14.3610(18)	7.9416(11)	13.825(8)
A	104.147(14)	90	90	95.96(10)
B	95.793(13)	90	91.047(5)	100.66(8)
Γ	98.240(13)	90	90	100.54(6)
U/A^3	1241.7(2)	1051.2(3)	1117.0(3)	1032.4(14)
Z	2	4	4	2
μ/cm^{-1}	17.73	38.78	36.51	37.52
Reflections collected	9104	12853	13382	8540
Independent reflections	4483	1926	2031	4089
R_{int}	0.0995	0.0364	0.0347	0.0793
R1	0.0758	0.0250	0.0229	0.0884
wR2 [$I > 2\sigma(I)$]	0.1592	0.0482	0.0819	0.2546

Table S3. Details of the x-ray data collections and refinements for compounds **10a**, **10b**, **10c** and **10d**

Compound	**10a**	**10b**	**10c**	**10d**
Formula	$C_{22}H_{14}F_5N_3O_3SSe$	$C_{23}H_{15}Cl_3F_5N_3O_3SSe$	$C_{24}H_{18}F_5N_3O_5SSe$	$C_{23}H_{16}F_5N_3O_3SSe$
M	574.38	693.76	634.44	588.41
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	P-1	$P2_1/c$	$P2_1/c$
a/Å	12.9213(9)	7.4201(5)	18.2430(12)	10.2003(7)
b/Å	7.5643(5)	12.6297(9)	7.5672(5)	17.8940(13)
c/Å	22.5143(15)	14.6868(11)	20.0832(2)	12.5877(9)
A	90	96.558(6)	90	90
B	96.433(7)	90.345(6)	116.938(6)	95.325(3)
Γ	90	95.925(6)	90	90
U/A^3	2186.7(3)	1359.82(17)	2471.5(4)	2287.6(3)
Z	4	2	4	4
μ/cm^{-1}	18.87	18.18	16.85	18.06
Reflections collected	18254	11817	19961	16920
Independent reflections	4005	4925	4465	4177
R_{int}	0.0675	0.0489	0.0558	0.0839
R1	0.0237	0.0312	0.0601	0.0407
wR2 [$I > 2\sigma(I)$]	0.0619	0.0831	0.1697	0.0771

3. Selected Crystallographic Bond Lengths and Angles compounds 2a, 2b, 2c, 3, 4, 6, 7 and 9, 10a, 10b, 10c and 10d

Table S4. Selected bond lengths (Å) and angles (˚) for molecular structures of **2a**, **2b**, **2c** and **4**

	2a	**2b**	**2c**	**4**
Se(1)-C(2)	1.889(2)	1.896(2)	1.893(3)	1.866(8)
C(2)-N(3)	1.370(3)	1.358(3)	1.354(4)	1.377(9)
N(3)-C(4)	1.407(3)	1.419(3)	1.417(4)	1.416(9)
C(4)-C(5)	1.335(3)	1.328(3)	1.333(5)	1.337(11)
Se(1)-C(5)	1.877(3)	1.879(3)	1.876(4)	1.865(8)
C(2)-N(6)	1.302(3)	1.316(3)	1.309(4)	1.314(9)
N(6)-C(7)	1.368(3)	1.366(3)	1.373(4)	1.380(9)
O(7)-C(7)	1.235(3)	1.242(3)	1.236(4)	1.237(9)
C(2)-Se(1)-C(5)	86.23(10)	85.83(10)	85.86(14)	86.0(3)
Se(1)-C(5)-C(4)	113.0(2)	113.40(18)	113.2(3)	113.8(6)
C(5)-C(4)-N(3)	114.1(2)	113.9(2)	113.9(3)	113.5(7)
C(4)-N(3)-C(2)	117.02(19)	116.91(18)	116.8(3)	115.5(6)
N(3)-C(2)-Se(1)	109.59(17)	109.98(15)	110.2(2)	111.1(5)
Se(1)-C(2)-N(6)	128.08(17)	127.48(17)	127.6(3)	127.9(6)
C(2)-N(6)-C(7)	115.60(19)	115.36(19)	115.3(3)	115.7(6)
N(6)-C(7)-O(7)	124.5(2)	123.7(2)	123.7(3)	123.3(7)
N(3)-C(2)-N(6)	122.3(2)	122.5(2)	122.2(3)	121.0(7)

Table S5. Selected bond lengths (Å) and angles (˚) for molecular structures of **10a**, **10b**, **10c** and **10d**

	10a	**10b**	**10c**	**10d**
Se(1)-C(2)	1.8748(17)	1.884(2)	1.893(6)	1.887(3)
C(2)-N(3)	1.367(3)	1.359(3)	1.382(7)	1.368(4)
N(3)-C(4)	1.415(2)	1.414(3)	1.414(7)	1.413(4)
C(4)-C(5)	1.345(3)	1.341(3)	1.331(9)	1.328(5)
Se(1)-C(5)	1.871(2)	1.870(2)	1.881(6)	1.863(4)
C(2)-N(6)	1.312(2)	1.309(3)	1.299(8)	1.309(4)
N(6)-C(7)	1.360(3)	1.360(3)	1.367(8)	1.370(4)
O(7)-C(7)	1.239(2)	1.240(3)	1.231(8)	1.245(4)
C(2)-Se(1)-C(5)	85.84(8)	85.72(9)	85.8(3)	85.61(16)
Se(1)-C(5)-C(4)	113.62(14)	113.73(17)	113.7(5)	114.3(3)
C(5)-C(4)-N(3)	113.33(17)	113.2(2)	114.2(5)	113.5(3)
C(4)-N(3)-C(2)	116.16(15)	116.71(17)	116.1(5)	116.3(3)
N(3)-C(2)-Se(1)	111.02(13)	110.61(15)	110.2(4)	110.3(3)
Se(1)-C(2)-N(6)	127.68(15)	128.17(16)	127.6(4)	127.5(3)
C(2)-N(6)-C(7)	116.83(16)	116.89(19)	116.5(5)	115.0(3)
N(6)-C(7)-O(7)	125.22(18)	125.2(2)	125.0(6)	124.9(3)
N(3)-C(2)-N(6)	121.28(16)	121.29(18)	122.2(5)	122.2(3)

Selected selected bond lengths (Å), angles (°) and torsion angles (°) for compound 3: Se(2)-C(2) 1.8345(5), N(1)-C(2) 1.332(6), N(3)-C(2) 1.383(6), N(3)-C(4) 1.406(6), C(4)-O(4) 1.225(5), C(4)-C(11) 1.465(7); Se(2)-C(2)-N(1) 124.2(4), Se(2)-C(2)-N(3) 117.8(3), N(1)-C(2)-N(3) 118.0(4), C(2)-N(3)-C(4) 128.3(4), N(3)-C(4)-O(4) 120.1(4), O(4)-C(4)-C(11) 123.4(4), N(3)-C(4)-C(11) 116.5(4); C(5)-N(1)-C(2)-N(3) -175.8(4).

Selected bond lengths (Å) and angles (˚) for compound 6: N(1)-C(1) 1.128(5), C(1)-C(2) 1.497(5), C(2)-N(3) 1.440(4), N(3)-C(4) 1.380(5); N(1)-C(1)-C(2) 178.6(4), C(1)-C(2)-N(3) 109.2(3), C(2)-N(3)-C(4) 127.4(3).

Selected bond lengths (Å) and angles (˚) for compound 7: N(1)-C(10) 1.37293, N(1)-C(2) 1.468(3), C(2)-C(3) 1.503(3), C(3)-C(4) 1.334(3); N(1)-C(2)-C(3) 109.18(18), C(2)-C(3)-C(4) 125.3(2), C(3)-C(4)-C(5) 119.22(19), C(4)-C(5)-C(10) 118.09(19), C(5)-C(10)-N(1) 119.88(19).

Selected bond lengths (Å) and angles (°) for compound 9: Se(1)-Se(2) 2.397(3), C(5)-Se(1) 1.919(11), C(3)-Se(2) 1.890(15), C(5)-N(4) 1.325(14), C(3)-N(4) 1.320(15), C(5)-N(13) 1.371(14), N(13)-C(14) 1.356(14), O(14)-C(14) 1.226(13), C(3)-N(6) 1.337(17); C(5)-Se(1)-Se(2) 88.4(3), Se(1)-Se(2)-C(3) 88.5(4), Se(2)-C(3)-N(4) 122.0(11), Se(2)-C(3)-N(6) 118.7(9), C(3)-N(4)-C(5) 120.3(11), Se(1)-C(5)-N(4) 120.6(8), Se(1)-C(5)-N(13) 118.6(8), N(4)-C(5)-N(13) 120.8(10), C(5)-N(13)-C(14) 115.4(9), N(13)-C(14)-O(14) 123.37(10).